CHAPTER

6 Rates of Reaction

Specific Expectations

In this chapter, you will learn how to . . .

- D1.2 **analyze** the conditions required to maximize the efficiency of some common natural or industrial chemical reactions (6.2)
- D2.1 **use** appropriate terminology related to energy changes and rates of reaction (6.1, 6.2, 6.3)
- D2.8 **plan** and **conduct** an inquiry to determine how various factors affect the rate of a chemical reaction (6.2)
- D3.5 **explain**, using collision theory and potential energy diagrams, how factors such as temperature, the surface area of the reactants, the nature of the reactants, the addition of catalysts, and the concentration of the solution control the rate of a chemical reaction (6.2)
- D3.6 **describe** simple potential energy diagrams of chemical reactions (6.2, 6.3)
- D3.7 **explain**, with reference to a simple chemical reaction, how the rate of a reaction is determined by the series of elementary steps that make up the overall reaction mechanism (6.3)

Fireflies, a common sight on summer nights in Ontario, are members of the beetle family that send out flashes of bright light to attract a mate. A firefly's brightness is referred to as its bioluminescent intensity and is determined by the rate (speed) at which a specific chemical reaction occurs in its abdomen. Various factors affect the rate of a reaction. For example, the rate of the bioluminescent reaction in fireflies is increased by the enzyme *luciferase*. The greater the concentration of this enzyme, the faster the reaction occurs. The concentration of the reactants involved also affects the reaction rate. As the concentration of reactants increases, so does the rate of the reaction. Scientists can determine the rate at which the reaction takes place by measuring the firefly's bioluminescent intensity, which is directly related to the rate at which photons of light are emitted by the insect.

Launch Lab

Factors That Affect Reaction Rate

How do different factors affect the rate of a reaction? In this activity, you will measure the time for a piece of magnesium to "disappear" under various reaction conditions and convert reaction time to reaction rate.

Safety Precautions

- Wear safety eyewear and protective clothing throughout this activity.
- If any HCl(aq) gets on your skin, immediately flush with plenty of cold water.

Materials

- 60 mL 1.0 mol/L HCl(aq)
- 6 - 1 cm pieces of clean magnesium ribbon
- small magnesium pieces cut from magnesium ribbon
- small piece of zinc (same mass as magnesium)
- 30 mL of water
- ice water for cooling
- 7 test tubes
- 400 mL beaker
- 10 mL graduated cylinder
- timing device that measures seconds
- thermometer

Procedure

1. Prepare solutions of hydrochloric acid as outlined in the table below.
2. Carry out each reaction. In each trial, measure and record the time for the metal to "disappear." Measure and record the temperature of each trial.
3. Your teacher will tell you the mass of 100 cm of magnesium. Use this to determine the mass of magnesium used.

Questions

1. For each trial, convert reaction time to reaction rate of metal in mol/s.
2. What was the effect on reaction rate of **a.** using different concentrations of acid? **b.** using magnesium pieces instead of a strip? **c.** changing temperature? **d.** using zinc rather than magnesium?
3. Summarize the effects of concentration, temperature, and nature of reactants with respect to the rate at which the reaction occurred.

Data Table

Trial	Volume of 1.0 mol/L HCl(aq) (mL)	Volume of Water (mL)	Total Volume of HCl(aq) (L)	Concentration of HCl (mol/L)	Metal Reacted	Reaction Time (s)	Temperature (°C)
1	10	0			1 cm Mg		room temperature
2	7	3			1 cm Mg		room temperature
3	5	5			1 cm Mg		room temperature
4	3	7			1 cm Mg		room temperature
5	10	0			1 cm Mg		5
6	10	0			Mg pieces		room temperature
7	10	0			equal mass zinc		room temperature

SECTION 6.1

Chemical Reaction Rates

Key Terms

reaction rate

average rate of reaction

instantaneous rate of reaction

Some processes, such as the complete hardening (curing) of concrete and the conversion of graphite to diamond, can take years, or even millions of years, to complete. Others, such as the reaction in **Figure 6.1**, occur so quickly that they are measured in femtoseconds—one millionth of one billionth of a second, 10^{-15} s. What accounts for differences in the rate at which reactions occur? What factors affect reaction rates? Chemists investigate such questions. On a practical level, chemists also investigate reaction rates to design medications, improve techniques to control pollution, and develop more efficient methods in the food processing industry.

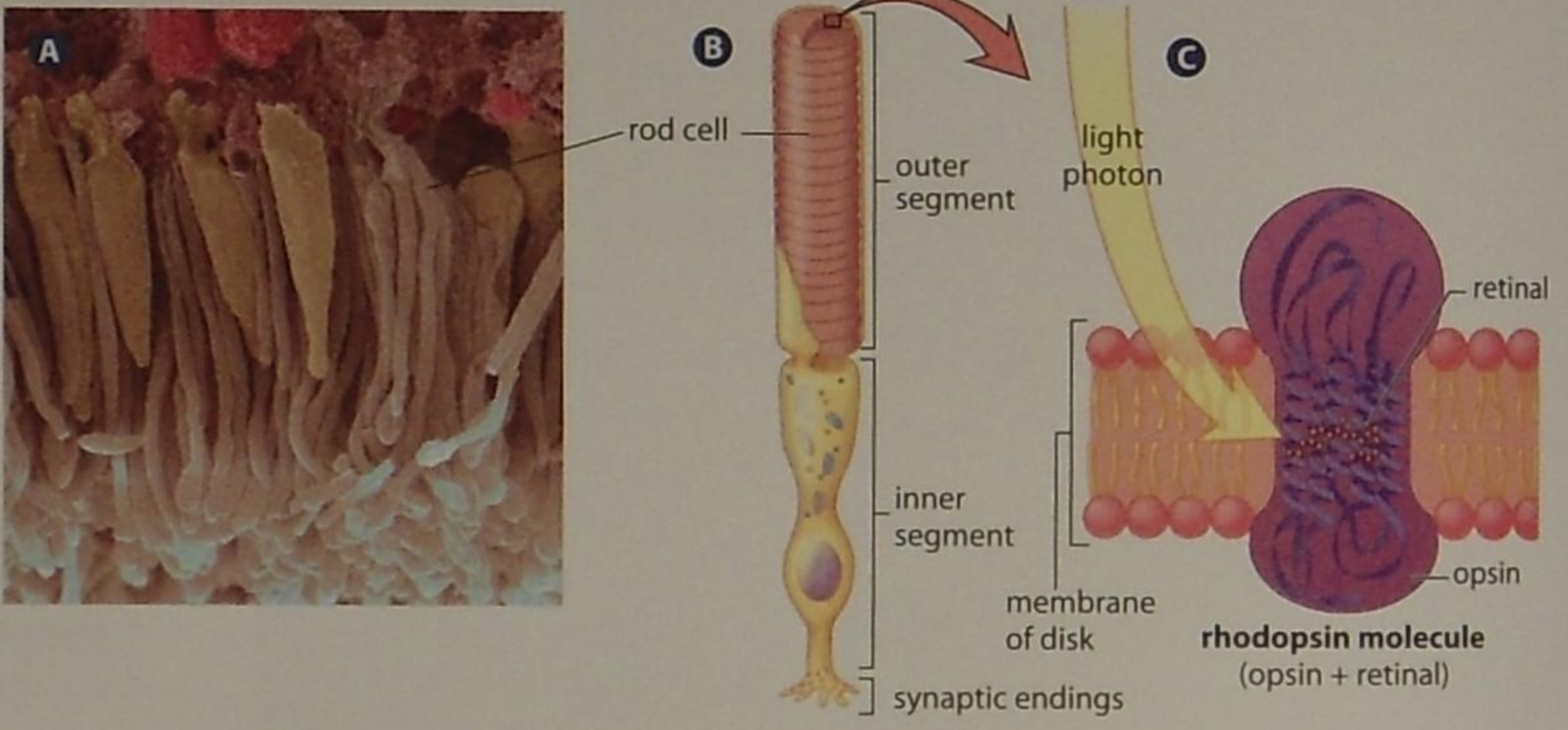


Figure 6.1 The retina, shown in this micrograph as a cross section (**A**), is located in the back of the eye. The rod cells of the retina (**B**) contain rhodopsin molecules, which are made up of the protein opsin and light-absorbing retinal (**C**). The first chemical event in vision occurs as rhodopsin absorbs a photon of light. This causes a portion of retinal to twist, changing its shape and triggering a series of reactions that lead to vision.

The field of chemistry that investigates the rate at which reactions occur is called *chemical kinetics*. You know the word "kinetics" from your study of thermodynamics. In the context of this chapter, kinetics refers to **reaction rates**—the change in the amount of reactants consumed or products formed over a given time interval. (Note that the term "rate of reaction" is often used when referring to reaction rates. Both mean the same thing.)

reaction rate the speed at which a reaction occurs, or the change in the amount of reactants consumed or products formed over a given time interval

Determining Reaction Rates

A rate is a description of a change in a quantity over a given time interval:

$$\text{rate} = \frac{\Delta\text{quantity}}{\Delta t}$$

For example, an Olympic male speed skater can skate a 5000 m race in about 6 min 15 s (6.25 min). This results in an average skating rate of 5000 m/6.25 min or 800 m/min (13.3 m/s). The rate in this case is determined based on the distance travelled divided by the time interval. The rate of a chemical reaction is the amount of reactants consumed or products formed divided by the time interval during which the change took place.

The reaction rate is usually given as a change in the concentration of a reactant or product per unit time. The symbol for the concentration of a compound in units of mol/L is a pair of square brackets, [ ], placed around the chemical formula. The reaction rate can be expressed as follows:

$$\text{reaction rate} = \frac{[\mathrm{A}]_{\text{final}} - [\mathrm{A}]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} = \frac{\Delta[\mathrm{A}]}{\Delta t}$$

Chemists determine the rate of a reaction by measuring the *increase* in concentration of a product or the *decrease* in concentration of a reactant. **Figure 6.2** shows the progress of a reaction in which compound A is converted into compound B. Each dot represents 1.0 mmol and the volume represents 1.0 L. Since there are 40 black dots in the first box, the initial concentration is 40 mmol/L (4.0×10^{-2} mol/L). Counting the black dots as the reaction progresses gives the data in **Table 6.1**.

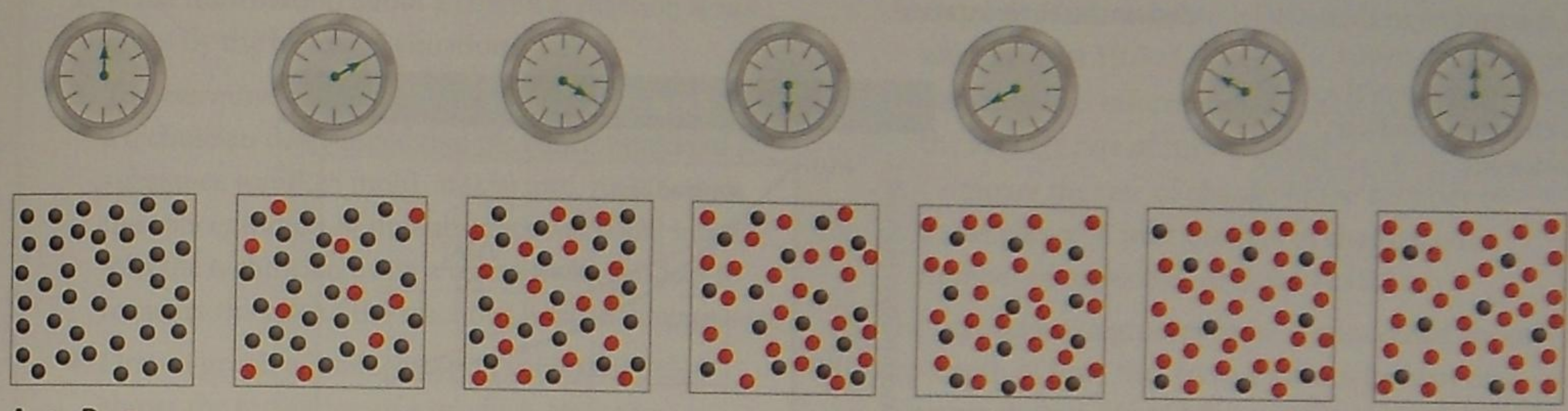


Figure 6.2 The black spheres represent 1.0 mmol of compound A, and the red spheres represent 1.0 mmol of compound B. The boxes show the progress of the reaction A ⟶ B every 10 s for an interval of 60 s.

Table 6.1 Concentration of A in Millimoles per Litre

Time (s)	[A] (mmol/L)
0.0	40.0
10.0	30.0
20.0	22.0
30.0	17.0
40.0	12.0
50.0	9.0
60.0	7.0

Figure 6.3 is a graph of the data in **Figure 6.2**. The concentrations of A and B are plotted against time. The reaction rate in terms of both the decrease in A and the increase in B can be obtained from the graph.

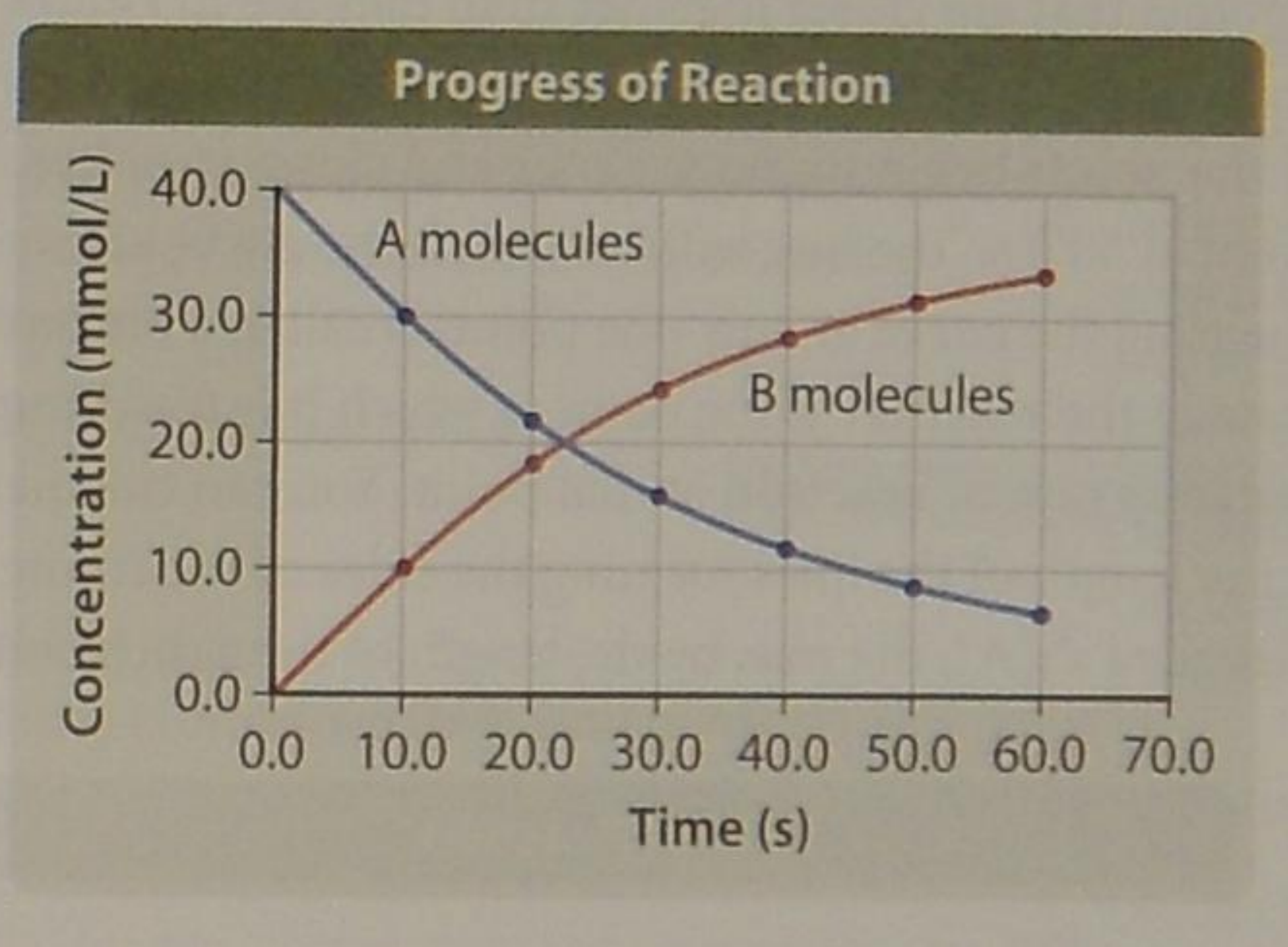


Figure 6.3 As the reaction A ⟶ B progresses, the number of molecules of A decreases, and the number of molecules of B increases. This graph represents the rate of the chemical reaction in an easily observable way.

The reaction rate in terms of the increase in the concentration of compound B can be expressed as follows:

$$\text{reaction rate} = \frac{\Delta[\text{B}]}{\Delta t}$$

Because the concentration of A is decreasing, the value of $\Delta[\text{A}]$ will be negative. To represent the reaction rate as a positive number, $\Delta[\text{A}]$ must be multiplied by -1. Therefore, the reaction rate in terms of the reactant, A, is expressed as follows:

$$\text{reaction rate} = -\frac{\Delta[\text{A}]}{\Delta t}$$

Average and Instantaneous Reaction Rates

average rate of reaction the change in the concentration of a reactant or product per unit time over a given time interval as a chemical reaction proceeds

Notice from the data on the previous page that the reaction rate between 10.0 s and 20.0 s is lower than the reaction rate between 0.0 s and 10.0 s. Because these two reactions occur over a period of time, both are considered **average rates of reaction**. A reaction rate calculated for any time interval is an average rate of reaction. As shown in **Figure 6.4**, an average rate of reaction is equal to the slope of a line drawn between the two points that define the time interval.

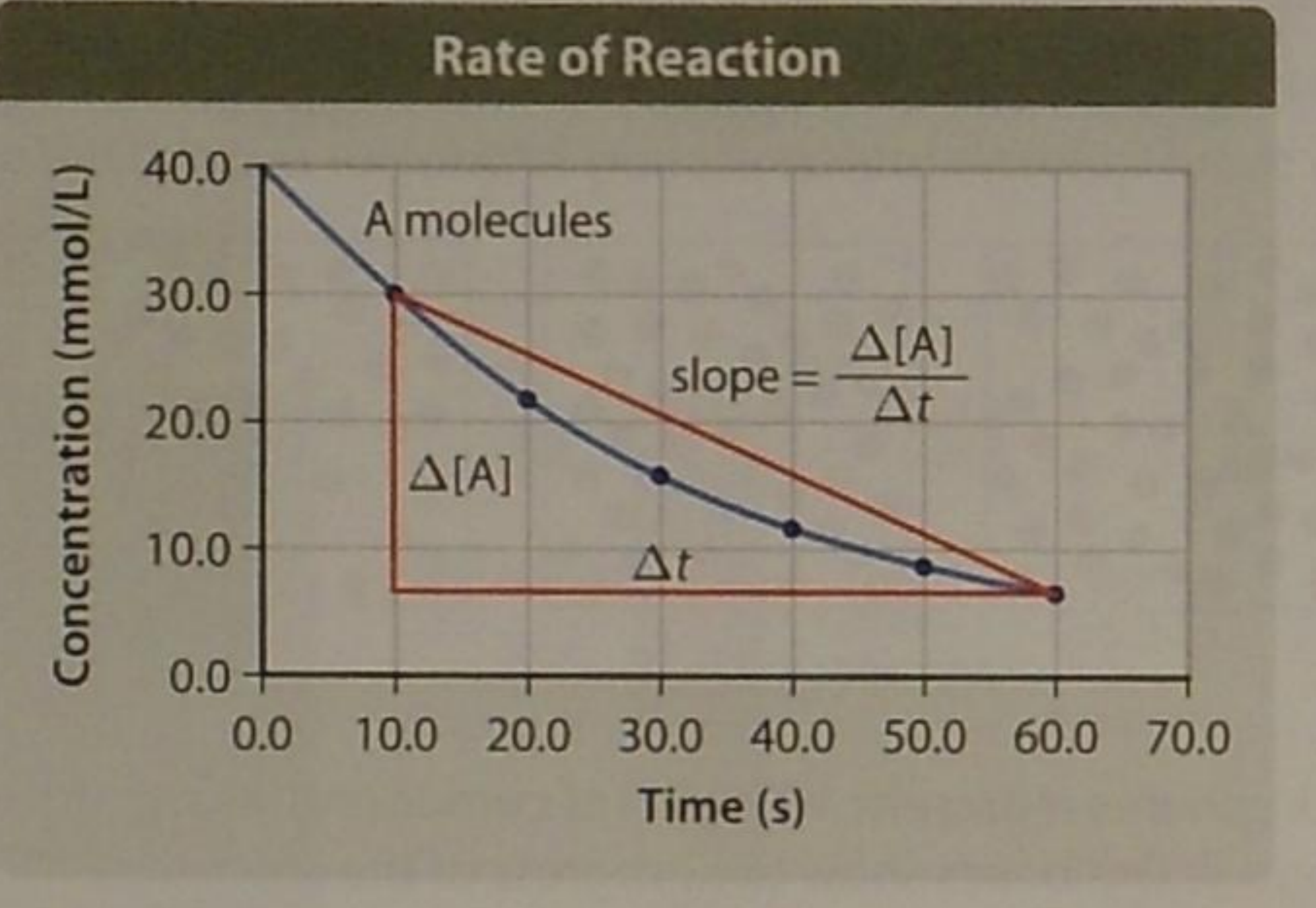


Figure 6.4 The average rate of a reaction is equal to the slope of a line between two points on the curve. The slope of a line is defined as the rise (vertical change) over the run (horizontal change).

Examine the slope drawn between 10.0 s and 30.0 s in **Figure 6.5**. Notice that as the line is drawn between points that are closer together than they are in **Figure 6.4**, the slope gets closer to the curve. Now imagine that the points at 40.0 s and 60.0 s have a slope drawn between them and the points begin to move closer and closer together. Eventually they will converge on the point at 50.0 s. The line will just touch the curve at one point. A line such as this, which is touching the curve at only one point, is called a tangent. The slope of the tangent gives the rate of the reaction at the point at which it is touching the curve. This is called the **instantaneous rate of reaction** at that point. You can calculate the instantaneous rate by measuring the length of the lines forming the sides of the triangle and dividing the length of the side labelled $\Delta[A]$, the rise, by the length of the side labelled Δt, the run.

instantaneous rate of reaction the rate of a chemical reaction at a particular point in time

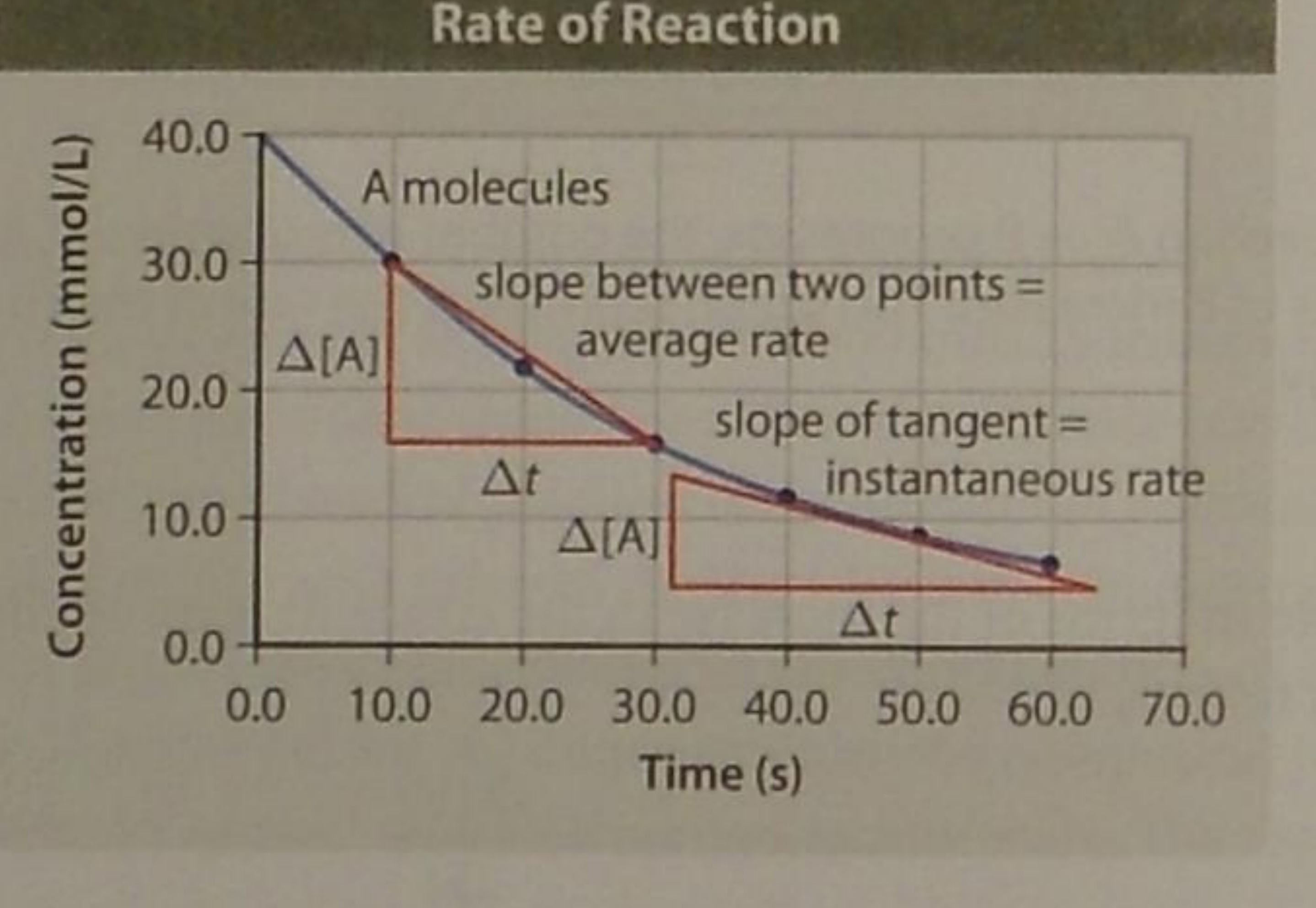


Figure 6.5 The slope of a line between two separate points on a concentration vs. time curve is the average rate of reaction. When a slope is drawn between two points and then the points are brought closer together until they converge to one point, the line becomes a tangent and the slope is the instantaneous rate of reaction.

Learning Check

1. What type of data could be used to determine the rate of the reaction for the chemical change that occurs when acid rain dissolves limestone and releases carbon dioxide?
2. What information about a chemical reaction is not given by the balanced equation?
3. To determine the average rate of a chemical reaction, a technician determined that the concentration of a substance was 0.25 mol/L at 0.50 min. At 2.00 min, the concentration of the substance was 0.420 mol/L. Was the technician using a reactant or a product to measure the rate of the reaction? Explain your answer.
4. Draw a graph of concentration versus time that shows the formation of a product. Near the centre of your graph, draw a tangent to the curve. Explain how you would use the tangent to find the instantaneous rate of the reaction at the time indicated by the tangent.
5. Refer to **Figure 6.2**, which shows information about the rate of the reaction A $\rightarrow$ B.
   a. If each dot represents one molecule, how many molecules of A remain after the first 10.0 s has elapsed? How many molecules of B have formed after the first 10.0 s?
   b. How can this information be used to determine the average rate of the reaction?
   c. Compare the rate of change in the number of molecules of A with the rate of change in the number of molecules of B at $t = 10.0$ s.
6. The manager of a grocery store is concerned about the length of time that fresh fruit can be kept on the store shelves. Would the manager be concerned about the instantaneous rate or the average rate at which the fruit spoils? Explain your answer.

Activity 6.1 Calculating Reaction Rates

In this activity, you will examine rate of reaction data for the decomposition of chlorine oxide, $ClO(g)$, which is involved in the depletion of ozone in Earth's upper atmosphere. At room temperature, chlorine oxide decomposes rapidly according to the following equation:

$$2ClO(g) \rightarrow Cl_2(g) + O_2(g)$$

Procedure

1. For the data provided in the table below, use graph paper or spreadsheet software to plot (and print) a labelled graph of the concentration of chlorine oxide (y-axis) vs. time (x-axis). Provide a descriptive title for your graph.

Reaction Data

Time (s)	[ClO] (mol/L)
0.12×10^{-3}	8.49×10^{-6}
0.96×10^{-3}	7.10×10^{-6}
2.24×10^{-3}	5.79×10^{-6}
3.20×10^{-3}	5.20×10^{-6}
4.00×10^{-3}	4.77×10^{-6}

2. On your graph, draw a straight line from the point at $t = 0.12 \times 10^{-3}$ s to the point at $t = 4.00 \times 10^{-3}$ s.
3. Additionally, draw a *tangent* to the curve at $t = 0.12 \times 10^{-3}$ s and at $t = 4.00 \times 10^{-3}$ s.
4. Determine the slope of the line drawn in step 2, with proper units; pay attention to significant digits. Calculate and record the *average* rate of the reaction over the given time interval.
5. Determine the slope of each tangent, with proper units. Calculate and record the instantaneous reaction rate at $t = 0.12 \times 10^{-3}$ s and at $t = 4.00 \times 10^{-3}$ s?

Questions

1. Explain how you know that this is a very fast reaction.
2. Why are the units for the average rate and the instantaneous rate of the reaction the same?
3. Explain how it is possible that two students could use the table data to determine different average reaction rates.
4. Propose an explanation for the different instantaneous reaction rates obtained at $t = 0.12 \times 10^{-3}$ s and at $t = 4.00 \times 10^{-3}$ s.
5. Why does the graph become more level as the reaction progresses?

Expressing Reaction Rates in Terms of Reactants or Products

By measuring the rate of change in the quantity of just one reactant or product in a chemical reaction, you can calculate the rate of change of all the other reactants and products involved in the reaction. The calculation is based on the coefficients in the balanced chemical equation that give the mole ratios for the components in the reaction. Consider, for example, hydrazine, $N_2H_4(\ell)$, which can decompose as follows:

$$3N_2H_4(\ell) \rightarrow 4NH_3(g) + N_2(g)$$

Note that for every 3 mol $N_2H_4(\ell)$ consumed per unit time in the reaction, 1 mol of nitrogen, $N_2(g)$, and 4 mol of ammonia, $NH_3(g)$, are formed. Mathematically, this can be stated as follows:

$$\frac{\text{rate of consumption of } N_2H_4(\ell)}{\text{rate of production of } N_2(g)} = \frac{3}{1} = \frac{-\frac{\Delta[N_2H_4]}{\Delta t}}{\frac{\Delta[N_2]}{\Delta t}}$$

$$\frac{\frac{\Delta[N_2]}{\Delta t}}{1} = \frac{-\frac{\Delta[N_2H_4]}{\Delta t}}{3}$$

or

$$\frac{\Delta[N_2]}{\Delta t} = -\left(\frac{1}{3}\right)\left(\frac{\Delta[N_2H_4]}{\Delta t}\right)$$

Similarly, for every 3 mol $N_2H_4(\ell)$ consumed in the reaction, 4 mol $NH_3(g)$ is formed. The mole ratio of ammonia to hydrazine is therefore 4:3. Using the same reasoning as was used above, you can express the rate of formation of $NH_3(g)$ relative to $N_2H_4(\ell)$:

$$\frac{\Delta[NH_3]}{\Delta t} = -\left(\frac{4}{3}\right)\left(\frac{\Delta[N_2H_4]}{\Delta t}\right)$$

Use the Sample Problem and Practice Problems below to practise calculating reaction rates.

Sample Problem

Calculating an Average Reaction Rate

Problem

In a reaction between butyl chloride, $C_4H_9Cl(aq)$, and water, the concentration of butyl chloride is 2.2×10^{-1} mol/L at the beginning of the reaction. At 4.00 s, the concentration of butyl chloride is 1.0×10^{-1} mol/L. Calculate the average reaction rate, in terms of butyl chloride, over the first 4.00 s of the reaction.

What Is Required?

You need to calculate the average rate at which butyl chloride is consumed during the first 4.00 s of the reaction between butyl chloride and water.

What Is Given?

You know the initial time: $t_{\text{initial}} = 0.00$ s
You know the final time: $t_{\text{final}} = 4.00$ s
You know the initial concentration of butyl chloride: $[C_4H_9Cl]_{\text{initial}} = 2.2 \times 10^{-1}$ mol/L
You know the final concentration of butyl chloride: $[C_4H_9Cl]_{\text{final}} = 1.0 \times 10^{-1}$ mol/L

Plan Your Strategy	Act on Your Strategy
Write the equation for the average rate of decrease of butyl chloride.	$\text{average rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = \frac{[C_4H_9Cl]_{final} - [C_4H_9Cl]_{initial}}{t_{final} - t_{initial}}$
Substitute the numerical values into the equation. Solve the equation.	$= -\left(\frac{1.0 \times 10^{-1}\ \frac{mol}{L} - 2.2 \times 10^{-1}\ \frac{mol}{L}}{4.00\ s - 0.0\ s}\right)$ $= -\left(\frac{-1.2 \times 10^{-1}\ \frac{mol}{L}}{4.00\ s}\right)$ $= 3.0 \times 10^{-2}\ \frac{mol}{L{\cdot}s}$ The average rate at which butyl chloride is consumed during the reaction is 3.0×10^{-2} mol/L·s.

Check Your Solution

The average reaction rate is reasonable given the initial and final concentrations of butyl chloride. The answer is correctly expressed in three significant digits. The answer is expressed in units of mol/L·s, which is correct.

Sample Problem

Determining Reaction Rates in Terms of Products and Reactants

Problem

Dinitrogen pentoxide, $N_2O_5(g)$, decomposes to form nitrogen dioxide and oxygen, according to the following equation: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

$NO_2(g)$ is produced at a rate of 5.00×10^{-6} mol/L·s.

a. What is the rate of decomposition of $N_2O_5(g)$?

b. What is the corresponding rate of formation of $O_2(g)$?

What Is Required?

Because $N_2O_5(g)$ is a reactant, you need to calculate its rate of decomposition. $O_2(g)$ is a product, so you need to determine its rate of formation.

What Is Given?

You know the rate of formation of nitrogen dioxide: $\text{rate} = \frac{\Delta[NO_2]}{\Delta t} = 5.00 \times 10^{-6}$ mol/L·s

You know the balanced chemical equation for the reaction.

Plan Your Strategy	Act on Your Strategy
a. Determine the ratio of $N_2O_5(g)$ to $NO_2(g)$.	2 mol N_2O_5 is decomposed for every 4 mol NO_2 formed, or $\frac{N_2O_5}{NO_2} = \frac{2}{4} = \frac{1}{2}$
Use the coefficients in the balanced chemical equation to determine the relative rate of decomposition of $N_2O_5(g)$.	For every mole of NO_2 that is formed, $\frac{1}{2}$ mol N_2O_5 is decomposed.
Write the equation for the rate of decomposition of $N_2O_5(g)$ relative to the rate of formation of $NO_2(g)$.	$\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\left(\frac{\Delta[NO_2]}{\Delta t}\right)$
Substitute the numerical values into the equation and solve the equation.	$\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\left(5.00 \times 10^{-6}\ \frac{mol}{L{\cdot}s}\right)$ $= 2.50 \times 10^{-6}\ \frac{mol}{L{\cdot}s}$ The rate of consumption of $N_2O_5(g)$ is 2.50×10^{-6} mol/L·s.

Continued on next page

b. Determine the ratio of $O_2(g)$ to $NO_2(g)$.	1 mol O_2 is formed for every 4 mol NO_2 formed, or $\frac{O_2}{NO_2} = \frac{1}{4}$
Use the coefficients in the balanced equation to determine the relative rate of decomposition of $N_2O_5(g)$.	For every mole of NO_2 formed, $\frac{1}{4}$ mol O_2 is formed.
Write the equation for the rate of decomposition of $N_2O_5(g)$ relative to the rate of formation of $NO_2(g)$.	$\frac{\Delta [O_2]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta [NO_2]}{\Delta t}\right)$
Substitute the numerical values into the equation and solve the equation.	$\frac{\Delta [O_2]}{\Delta t} = \frac{1}{4}\left(5.0 \times 10^{-6} \frac{mol}{L{\cdot}s}\right)$ $= 1.25 \times 10^{-6} \frac{mol}{L{\cdot}s}$ The rate of production of $O_2(g)$ is 1.25×10^{-6} mol/L·s.

Check Your Solution

From the coefficients in the balanced chemical equation, you can see that the rate of decomposition of $N_2O_5(g)$ is $\frac{2}{4}$ or $\frac{1}{2}$, which is also the rate of formation of $NO_2(g)$. The rate of formation of $O_2(g)$ is $\frac{1}{2}$ the rate of decomposition of $N_2O_5(g)$.

Practice Problems

1. In the reaction $A + 2B \rightarrow 3C + 4D$, the initial concentration of A was 0.0415 mol/L, and after 14.7 min the concentration of A was 0.0206 mol/L. What is the average rate of consumption in moles per litre per second of reactant B?

2. Calculate the average rate of a reaction, given the following data:

Reaction Data

Time (s)	Concentration (mol/L)
60	5.00×10^{-2}
85	3.25×10^{-2}

3. For the reaction shown below, the average rate of formation of $CO_2(g)$ is 5.50×10^{-4} mol/s.

$$Br_2(aq) + HCOOH(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

a. What amount in moles of $CO_2(g)$ is formed in 5.00 min?

b. How does this compare with the amount of $Br_2(aq)$ that reacts in the same time?

4. The concentration of a reactant is 4.0×10^{-2} mol/L at $t = 2.0$ min. If the average rate of consumption of the reactant from $t = 1.5$ min to $t = 2.0$ min was 0.045 mol/L·s, what was the concentration of this reactant at $t = 1.5$ min?

5. A zinc electrode is immersed in dilute sulfuric acid at 35.0°C and the following reaction occurs:

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

The volume of $H_2(g)$ present at $t = 1.0$ min is 30.0 mL and at $t = 1.4$ min is 42.0 mL. What is the average rate of formation of $H_2(g)$ over this period of time measured in litres per second?

6. For the reaction shown below, the instantaneous rate of formation of $Br^-(aq)$ is 0.12 mol/L·s at $t = 2.0$ min.

$$3BrO^-(aq) \rightarrow BrO_3^-(aq) + 2Br^-(aq)$$

What are the instantaneous rates of formation of $BrO_3^-(aq)$ and consumption of $BrO^-(aq)$?

7. The data in the table below were obtained for the following reaction:

$$4HBr(g) + O_2(g) \rightarrow 2Br_2(g) + 2H_2O(g)$$

Reaction Data

Time (s)	[HBr] (mol/L)	[Br_2] (mol/L)
0.00	0.42	0.00
50.0	0.26	?

a. What is the average rate of consumption of HBr(g) over 50.0 s?

b. What is the molar concentration of $Br_2(g)$ at $t = 50.0$ s?

8. Consider the following reaction:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Over a period of 1.80 min, the average rate of formation of NO(g) is 1.04 mol/L·s.

What was the amount in moles of $O_2(g)$ consumed over this period of time?

9. A mass of 0.50 g of sodium metal reacts with water in 90.0 s.

$$2Na(s) + 2H_2O(\ell) \rightarrow 2NaOH(aq) + H_2(g) + \text{heat}$$

a. Express the rate of consumption of Na(s) in moles per second.

b. Calculate the rate at which $H_2(g)$ is generated, in litres per second, at 30.0°C and 102.4 kPa. Assume that hydrogen is an ideal gas.

10. For the reaction shown below, the instantaneous change in concentration of NO(g) is 1.4 mol/L·s.

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

What is the rate at which $Cl_2(g)$ is consumed and the rate at which NOCl(g) is formed at this time?

Methods for Measuring Rates of Reaction

Chemists collect the data required to determine a reaction rate in a variety of ways, but all methods involve monitoring the rate at which a reactant is consumed or the rate at which a product is formed. The choice of method to be used depends on which reactant or product is measurable. For example, if a reactant or product has a specific colour, its consumption or formation can be measured quantitatively with a spectrophotometer, an instrument that measures the absorbance of light at any specific wavelength. If a gaseous product is formed, the gas can be collected and the volume measured. The mass of the non-gaseous compounds can be measured using a balance as a gaseous product escapes.

For example, consider the chemical reaction between calcium carbonate, $CaCO_3(s)$, and hydrochloric acid, 2HCl(aq). One of the products of this reaction is carbon dioxide, as shown in the following chemical equation:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(\ell) + CO_2(g)$$

Measuring the Volume of Gas Produced

One method of measuring the rate of this reaction is to collect the carbon dioxide being formed and measure its volume. **Figure 6.6** shows one method for measuring a gas as it is being formed by a chemical reaction. The reaction vessel (flask) has been connected to a syringe with tubing. When the reaction begins, the plunger of the syringe is pushed all the way in. As the gas escapes, it goes into the syringe, pushing the plunger back. The scale on the syringe shows how much gas has been collected.

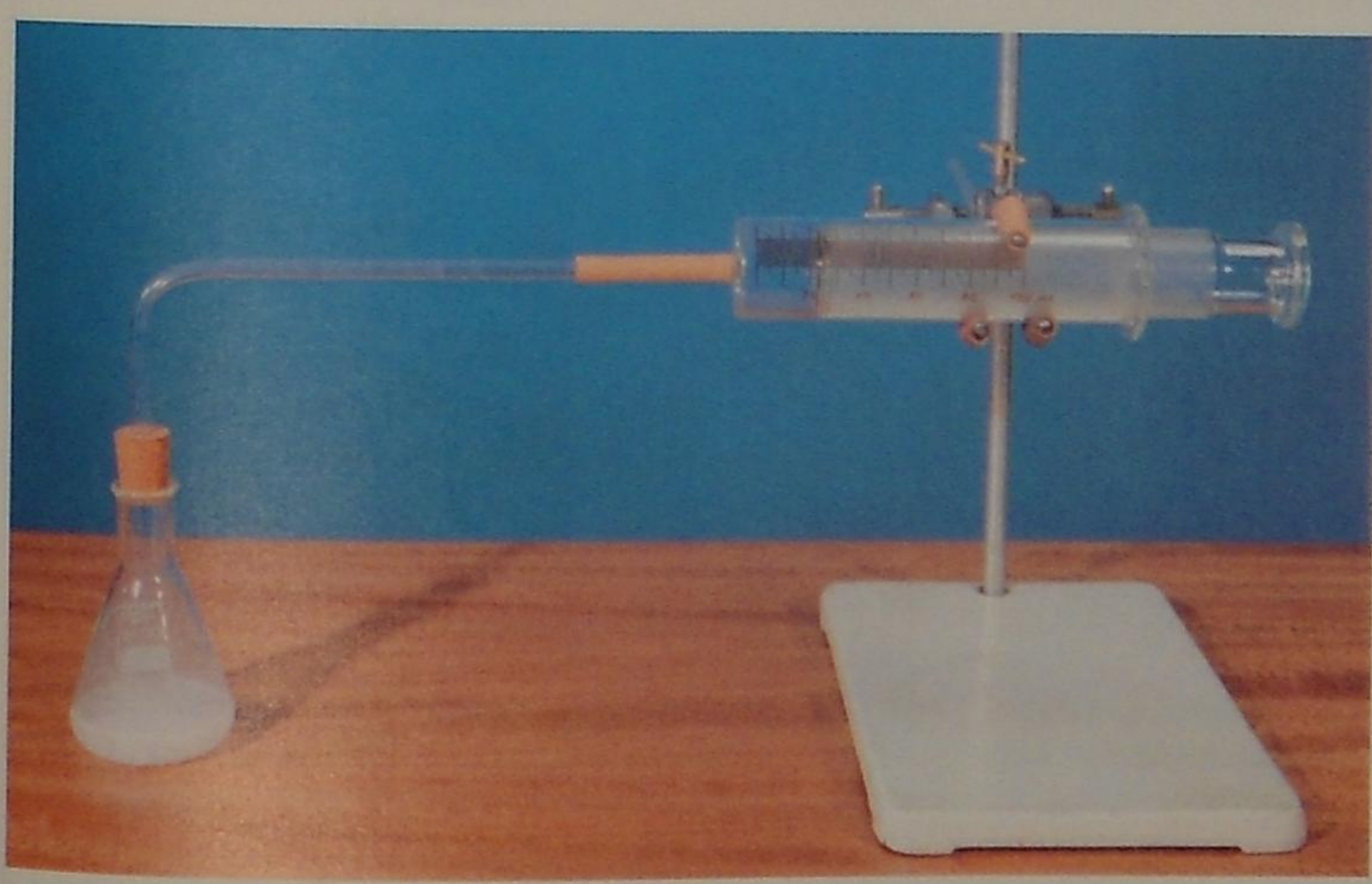


Figure 6.6 By measuring the increase in the volume of gas collected over time, the reaction rate can be determined.

Measuring the Remaining Mass

Another method for determining the rate of the chemical reaction between calcium carbonate and hydrochloric acid is to measure the decrease in mass that occurs as carbon dioxide escapes from an open container, as shown in **Figure 6.7**. The cotton wool in the opening of the flask prevents any liquid from splashing out as the solution bubbles up, but carbon dioxide easily escapes through the cotton wool. In general, the method shown in **Figure 6.7** works well for reactions that generate carbon dioxide or oxygen, but not for reactions that generate hydrogen, which has a much lower mass.

Table 6.2 summarizes some common methods for measuring reaction rates. Regardless of the method used to collect data, the rate would be reported in moles per second, requiring a conversion from the quantity measured into unit of moles.

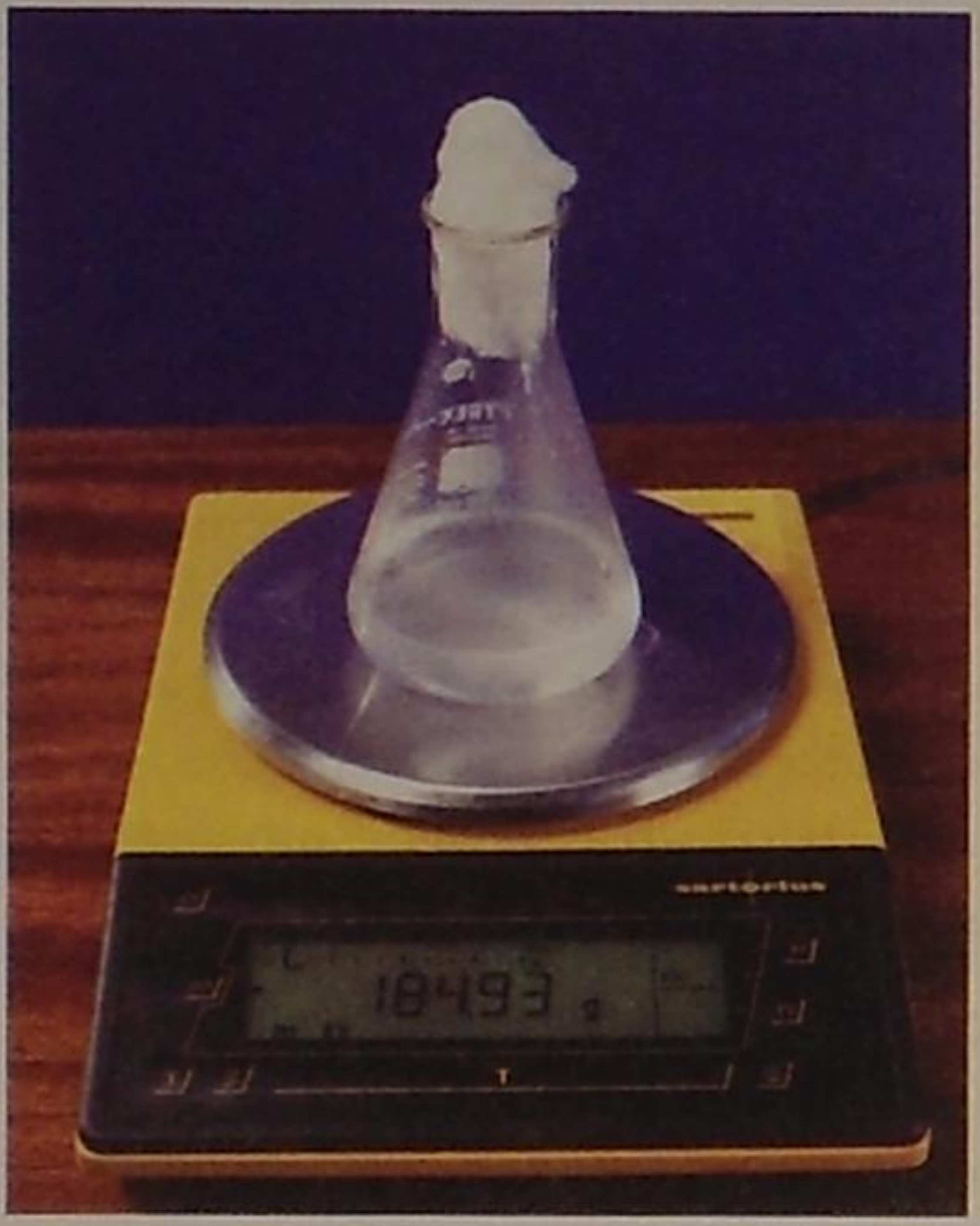


Figure 6.7 Calcium carbonate and hydrochloric acid are reacting in this flask. By measuring the loss in mass over time as carbon dioxide escapes, the reaction rate can be determined. ***Analyze** how the measurement of the rate of reaction might be affected if cotton wool were not used?*

Table 6.2 Methods for Measuring Rates of Chemical Reactions

Property Measured	Type of Data Collected	Typical Equipment Used	Equation for Determining Rate
Volume	Volume of gas formed	Gas syringe	$\text{rate} = \frac{\Delta \text{volume}}{\Delta t}$
Mass	Change in mass of a reactant or a product	Balance	$\text{rate} = \frac{\Delta \text{mass}}{\Delta t}$
Temperature	Increase in temperature as an exothermic reaction proceeds or decrease in temperature as an endothermic reaction proceeds	Thermometer	$\text{rate} = \frac{\Delta \text{temperature}}{\Delta t}$
Pressure	Change in pressure in a closed container as a gas is formed or consumed	Pressure sensor	$\text{rate} = \frac{\Delta \text{pressure}}{\Delta t}$
Colour	Change in the amount of light of a specific wavelength absorbed by a chemical compound; changes with the concentration of the compound	Spectrophotometer	$\text{rate} = \frac{\Delta \text{absorbance}}{\Delta t}$
pH	Change in concentration of H_3O^+ or OH^- ions as a reaction proceeds	pH meter	$\text{rate} = \frac{\Delta \text{pH}}{\Delta t}$
Electrical conductivity	Change in the concentration of dissolved ions as a reaction proceeds	Electrical conductivity probe	$\text{rate} = \frac{\Delta \text{conductivity}}{\Delta t}$

Calculating Reaction Rates from Experimental Data

After data have been collected, it must be used to calculate the reaction rate. For example, suppose that a technician measures both the volume of carbon dioxide released and the mass of the remaining solution for the reaction above, between calcium carbonate and hydrochloric acid. Because volumes of gases are affected by the temperature and pressure, the technician recorded these values when taking data. The following data were recorded:

$T = 291\text{ K}$ $\quad\quad\quad$ $\Delta m_{\text{solution}} = -47.0\text{ mg}$

$P = 102.1\text{ kPa}$ $\quad\quad\quad$ $\Delta t = 5.00\text{ min}$

$V_{CO_2} = 25.3\text{ mL}$

The calculations below show how to determine the average rate of the reaction from both the volume data and the mass data.

Calculating the rate from the volume of CO_2:

- Convert volume from mL to L.

$$25.3\,\cancel{\text{mL}}\left(\frac{1\text{ L}}{1000\,\cancel{\text{mL}}}\right) = 0.0253\text{ L}$$

- To find the amount in moles of a gas from a volume, use the ideal gas law and solve for n.

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$n = \frac{(102.1\,\cancel{\text{kPa}})(0.0253\,\cancel{\text{L}})}{\left(\frac{8.314\,\cancel{\text{kPa}}\cdot\cancel{\text{L}}}{\text{mol}\cdot\cancel{\text{K}}}\right)(291\,\cancel{\text{K}})}$$

$$= 1.0677 \times 10^{-3}\text{ mol}$$

- Use the amount in moles and the time to calculate the rate in mol/s.

$$\text{rate} = \frac{\Delta n}{\Delta t}$$

$$= \frac{1.0677 \times 10^{-3}\text{ mol}}{5\,\cancel{\text{min}}\left(\frac{60\text{ s}}{\cancel{\text{min}}}\right)}$$

$$= 3.559 \times 10^{-6}\,\frac{\text{mol}}{\text{s}}$$

$$= 3.56 \times 10^{-6}\,\frac{\text{mol}}{\text{s}}$$

Calculating the rate from the change in the mass of the solution:

- The decrease in the mass of the solution is the mass of the $CO_2(g)$ that escaped. Therefore, the mass of the $CO_2(g)$ was 47.0 mg.
- Determine the molar mass of $CO_2(g)$.

$$M_{CO_2} = M_C + 2M_O$$

$$= 12.01\,\frac{\text{g}}{\text{mol}} + 2\left(16.00\,\frac{\text{g}}{\text{mol}}\right)$$

$$= 44.01\,\frac{\text{g}}{\text{mol}}$$

- Determine the amount in moles from the mass and the molar mass.

$$n = \frac{m}{M}$$

$$= \frac{(47.0\,\cancel{\text{mg}})\left(\frac{1\,\cancel{\text{g}}}{1000\,\cancel{\text{mg}}}\right)}{44.01\,\frac{\cancel{\text{g}}}{\text{mol}}}$$

$$= 0.0010679\text{ mol}$$

- Use the amount in moles and the time to calculate the rate in moles per second.

$$\text{rate} = \frac{\Delta n}{\Delta t}$$

$$= \frac{1.0679 \times 10^{-3}\text{ mol}}{5\,\cancel{\text{min}}\left(\frac{60\text{ s}}{\cancel{\text{min}}}\right)}$$

$$= 3.5597 \times 10^{-6}\,\frac{\text{mol}}{\text{s}}$$

$$= 3.56 \times 10^{-6}\,\frac{\text{mol}}{\text{s}}$$

Notice that the same answer is obtained with both types of data. These data can be used to find the rate in terms of either the hydrochloric acid or calcium carbonate.

To use the other forms of data listed in **Table 6.2**, information that relates the form of data to amount in moles or concentration must be used. For example, when using absorbance data from a spectrophotometer, the absorbance of standard solutions of known concentrations will be measured at the wavelength at which the solution absorbs the most light. These measurements will be used to find the correct conversion factor for absorbance versus concentration. Similar methods can be found for the other forms of data.

Section 6.1 Review

Section Summary

- A reaction rate is the speed at which a chemical reaction proceeds. A reaction rate is measured by the change in the amount of reactants consumed or products formed over a given time interval.
- A reaction rate is always expressed as a positive value.
- The instantaneous rate of a reaction is the rate of the reaction at a particular point in time.
- The average rate of a chemical reaction is the change in the concentration of a reactant or product per unit time over a given time interval.
- Any measurable property that is related to a change in the amount of a reactant consumed or product formed during a chemical reaction can be used to determine the reaction rate.

Review Questions

1. K/U List four applications where an understanding of the rate of a reaction can benefit society.
2. K/U Answer the questions about reaction rates.
   a. Distinguish between the terms *instantaneous* rate of reaction and *average* rate of reaction.
   b. The concentrations of a product measured in mol/L are collected over time measured in seconds. How can these data be used to determine the instantaneous and average rates of the reaction?
   c. What are the units for the instantaneous rate and average rate that would come from using these data?
3. T/I A solution of copper(II) sulfate, $CuSO_4(aq)$, has a concentration of 0.50 mol/L. A piece of zinc metal is placed in the solution. After 280 s, the concentration of the $CuSO_4(aq)$ is 0.42 mol/L. At what average rate is the concentration of $CuSO_4(aq)$ changing over this period of time?
4. T/I A piece of metal initially has a mass of 6.29 g. Exactly 2 days later, it has corroded and the mass of the metal is now 6.18 g. Express the rate at which the metal corroded over this period of time in grams per second.
5. T/I As potassium chlorate decomposes, oxygen gas is released. The total volume of $O_2(g)$ produced is 88.4 mL. If the average rate of the formation of oxygen over the course of the reaction is 0.670 mL/s, how long did the reaction last?
6. T/I A graph of concentration vs. time for the formation of a product in a reaction has been plotted. The slope of the tangent to this graph was measured at two different time points: $t = 2.0$ min and $t = 5.0$ min. One slope is 4.5×10^{-2} mol/L·min and the other is 9.2×10^{-2} mol/L·min.
   a. What does the tangent represent?
   b. Which slope was measured at $t = 5$ min? Give a reason for your answer.
   c. Is it possible that these measurements could represent the consumption of the reactant? Give a reason for your answer.
7. C You and your lab partner are designing an investigation to determine the rate of the reaction between magnesium ribbon and a dilute acid.
   a. What questions would you ask in order to decide which is easier to measure: the instantaneous rate or the average rate of reaction?
   b. Which do you believe would be easier: determining the instantaneous rate or the average rate? Give a reason for your answer.
8. K/U Refer to **Figure 6.3**. What is happening in the reaction at the point in time where the two lines intersect?
9. C For the reaction shown below, all of AB is consumed.

   $$AB \rightarrow A + B$$

   Sketch a graph of concentration vs. time for the reactant and products as the reaction proceeds to completion.
10. C While working in groups to review the concepts related to rates of reactions, a statement is made that as a reaction slows down, the instantaneous rate and the average rate of a reaction are essentially the same. Do you agree with this statement? Explain your answer using a graph of concentration of product vs. time.
11. K/U In order to use the rate of change in the quantity of one substance in a reaction to determine the rate of change of another, what information must be known?
12. A For the reaction shown below, NO(g) is produced at a rate of 0.080 mol/L·s.

    $$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

    At this same point in time, what is the rate of consumption of $O_2(g)$ and the rate of formation of $H_2O(g)$?

SECTION 6.2 Collision Theory and Factors Affecting Rates of Reaction

Chemists propose that, for a reaction to occur, reacting particles (atoms, molecules, or ions) must collide with one another. This proposition, known as **collision theory**, is supported by the kinetic molecular theory of gases. Consider, for example, a 1 mL sample of gas at room temperature and standard atmospheric pressure. Chemists estimate that approximately 10^{28} collisions among gas molecules take place in the sample every second. If each collision resulted in a reaction, however, all the reactions would be complete in about a nanosecond (10^{-9} s). In fact, these reactions can occur much more slowly than this. Thus, it is reasonable to infer that only a small fraction of collisions between reactants results in a reaction.

Key Terms

collision theory
activation energy, E_a
activated complex
catalyst
enzyme

Effective Collisions

For a collision between reactants to result in a reaction, the collision must be *effective*. An effective collision—one that results in the formation of products—must satisfy both of the criteria (conditions) outlined below.

For a collision between reactant particles to be effective
1. the orientation of the reactants (the collision geometry) must be favourable; and
2. the collision must occur with sufficient energy.

collision theory the theory that a reaction occurs between two particles (atoms, molecules, or ions) if they collide at the correct orientation and with certain minimum energy

Effective Collision Criteria 1: The Correct Orientation of Reactants

In order for a reaction to occur, reacting particles must collide with the proper orientation relative to one another. This is known as having the correct *collision geometry*. The importance of proper collision geometry can be illustrated by the following reaction:

$$NO(g) + NO_3(g) \rightarrow 2NO_2(g)$$

Figure 6.8 shows five of the many possible ways in which nitrogen monoxide, NO(g), and nitrogen trioxide, $NO_3(g)$, can collide. Only *one* of the five possibilities has the correct collision geometry for a reaction to occur. As shown in the diagram, only a specific orientation of the two reactants before collision leads to the formation of two molecules of nitrogen dioxide, $NO_2(g)$. Notice that, in the effective collision, the angle at which the nitrogen atom in the nitrogen monoxide molecule is approaching the oxygen atom in the nitrogen trioxide molecule is the same angle as that formed in the nitrogen dioxide molecules.

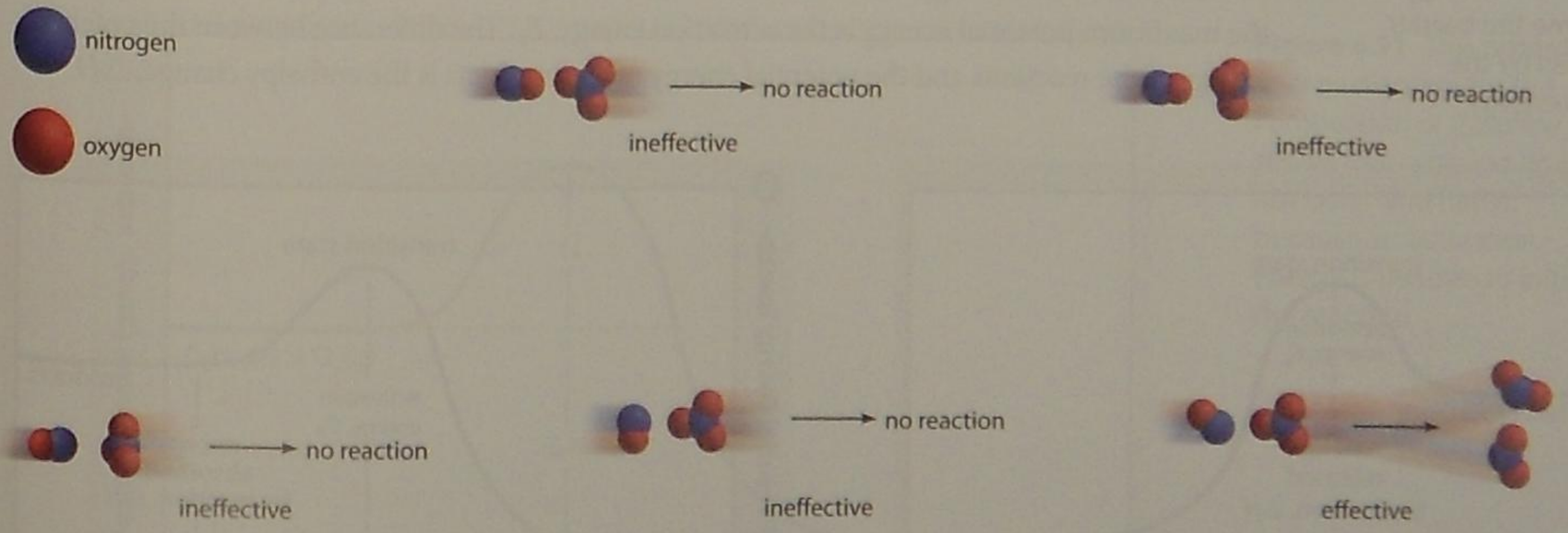


Figure 6.8 Only one of these possible orientations of NO(g) and $NO_3(g)$ relative to each other will lead to the formation of the product, $NO_2(g)$.
***Explain** why all but one of the collisions shown here are ineffective.*

activation energy, E_a the minimum amount of energy (collision energy) required to initiate a chemical reaction

Effective Collision Criteria 2: Sufficient Activation Energy

In addition to having the correct collision geometry, reactant particles must collide with one another with sufficient energy for a reaction to occur. In most reactions, only a small fraction of the total collisions have sufficient energy for a reaction to occur. The **activation energy, E_a**, of a reaction is the minimum collision energy required for the reaction to take place.

The collision energy depends on the kinetic energy of the colliding particles. Plotting the number of collisions between the particles in a substance at a given temperature against the kinetic energy of each collision gives a curve like the one in **Figure 6.9**. This type of distribution is called a *Maxwell-Boltzmann distribution*. The dotted line indicates the activation energy. The shaded part of the graph indicates the fraction of the total collisions that have energy equal to or greater than the activation energy. The activation energy is independent of temperature—that is, it does not change when temperature changes.

Suppose that a particular set of reactants collide 10 000 times per second, and the fraction of effective collisions is 1 reaction/50 collisions. The reaction rate could be expressed as 10 000 collisions/s × 1 reaction/50 collisions, or 200 reactions/s. This rate would change if either the number of collisions per second or the fraction of effective collisions changed. For example, if the fraction of effective collisions increased to 1 reaction/25 collisions, the reaction rate would double to 400 reactions/s.

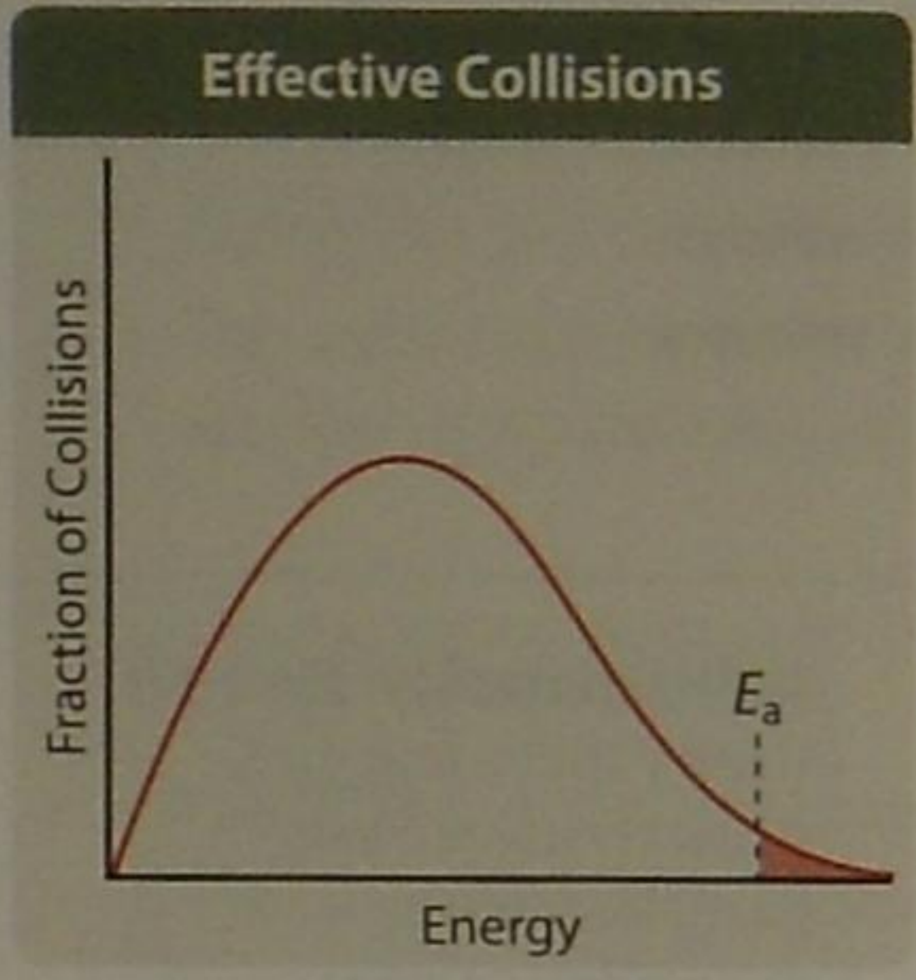


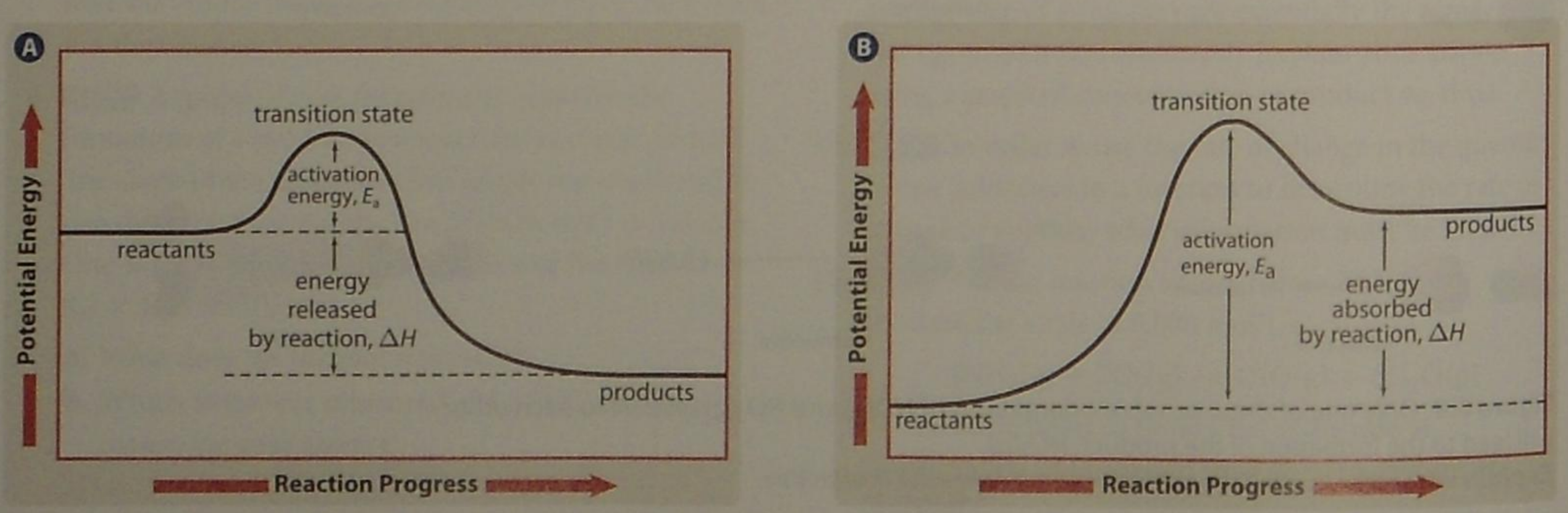
Figure 6.9 The area under a Maxwell-Boltzmann distribution curve represents the distribution of the kinetic energy of collisions at a given temperature. At any given temperature, only a small fraction of the molecules in a sample have enough kinetic energy to react.

Representing the Progress of a Chemical Reaction

The changes in potential energy during a chemical reaction can be represented using a potential energy diagram, as shown in **Figure 6.10**. On the left side of the curve, the reactants are approaching each other. Moving from left to right of the curve, the potential energy increases as the reactants get closer to each other. If the collision energy is not as great as the maximum potential energy at the top of the curve, the reactants cannot get close enough to have an effective collision, so they instead "bounce off" each other ineffectually. The small fraction of reactants that have sufficient kinetic energy will change in configuration and are then said to be in their *transition state*, somewhere between reactants and products. From the transition state, the process can go forward to form products or go backward and re-form the reactants. The products or the re-formed reactants will move apart. The collisions are effective only if the compound in the transition state breaks apart in the way that forms products.

In **Figure 6.10A**, the products have a lower energy than the reactants have. This decrease in potential energy means that energy was released in the reaction, so the reaction was exothermic. In **Figure 6.10B**, the products have more potential energy; thus, the reaction is endothermic, because it absorbed energy. The difference between the potential energy of the reactants and the maximum potential energy is the activation energy, E_a. The difference between the potential energy of the reactants and the potential energy of the products is the enthalpy change, ΔH.

Figure 6.10 Potential energy diagrams for an exothermic reaction (**A**) and an endothermic reaction (**B**). In both cases, a reaction can occur only if molecules collide with enough kinetic energy to overcome the barrier represented by the activation energy.



Learning Check

7. What criteria must be met in order to have an effective collision between reactant particles?
8. In 1 mL of a gas, there can be about 10^{28} collisions per second between reactant particles. With such a high number of collisions, you might expect all chemical reactions to go to completion instantaneously. Why does this not happen?
9. In order to have an effective collision, why is it necessary for the reactant particles to be properly oriented relative to one another?
10. Explain how you would know whether a reaction was exothermic or endothermic by examining a potential energy diagram that had no labels on it.
11. Answer these questions about activation energy.
    a. What is the meaning of the term *activation energy*, E_a?
    b. Reactions with a high E_a are generally slow at room temperature. Use collision theory to suggest an explanation for this statement.
12. List at least three characteristics of a reaction that you can determine from a potential energy diagram. Explain how you can determine those characteristics.

Activation Energy and Enthalpy

There is no way to predict the activation energy of a reaction from its enthalpy change. A highly exothermic reaction can have a very high activation energy and occur very slowly at room temperature. Conversely, a reaction may release very little heat, or even be endothermic, and still occur rapidly at room temperature. The enthalpy change of a reaction is determined only on the basis of the difference in the potential energy of the reactants and the products; it is independent of any process that occurs during the reaction.

The activation energy of a reaction is determined by analyzing the reaction rate at various temperatures. In general, reactions with low activation energies tend to proceed quickly at room temperature, regardless of whether they are endothermic or exothermic. However, exothermic or endothermic reactions with high activation energies tend to proceed slowly at room temperature.

Since gasoline is highly flammable, why does it not burst spontaneously into flames? The answer is that gasoline, which is mostly octane, requires a spark—a small *energy input*—to initiate combustion. The spark provides enough energy for a few octane and oxygen molecules to overcome the activation energy barrier. Once ignited, the gasoline continues to burn, because the energy released increases the kinetic energy of many other molecules, which can then overcome the activation energy barrier. Notice in **Figure 6.11** that the activation energy is relatively small compared with the enthalpy change.

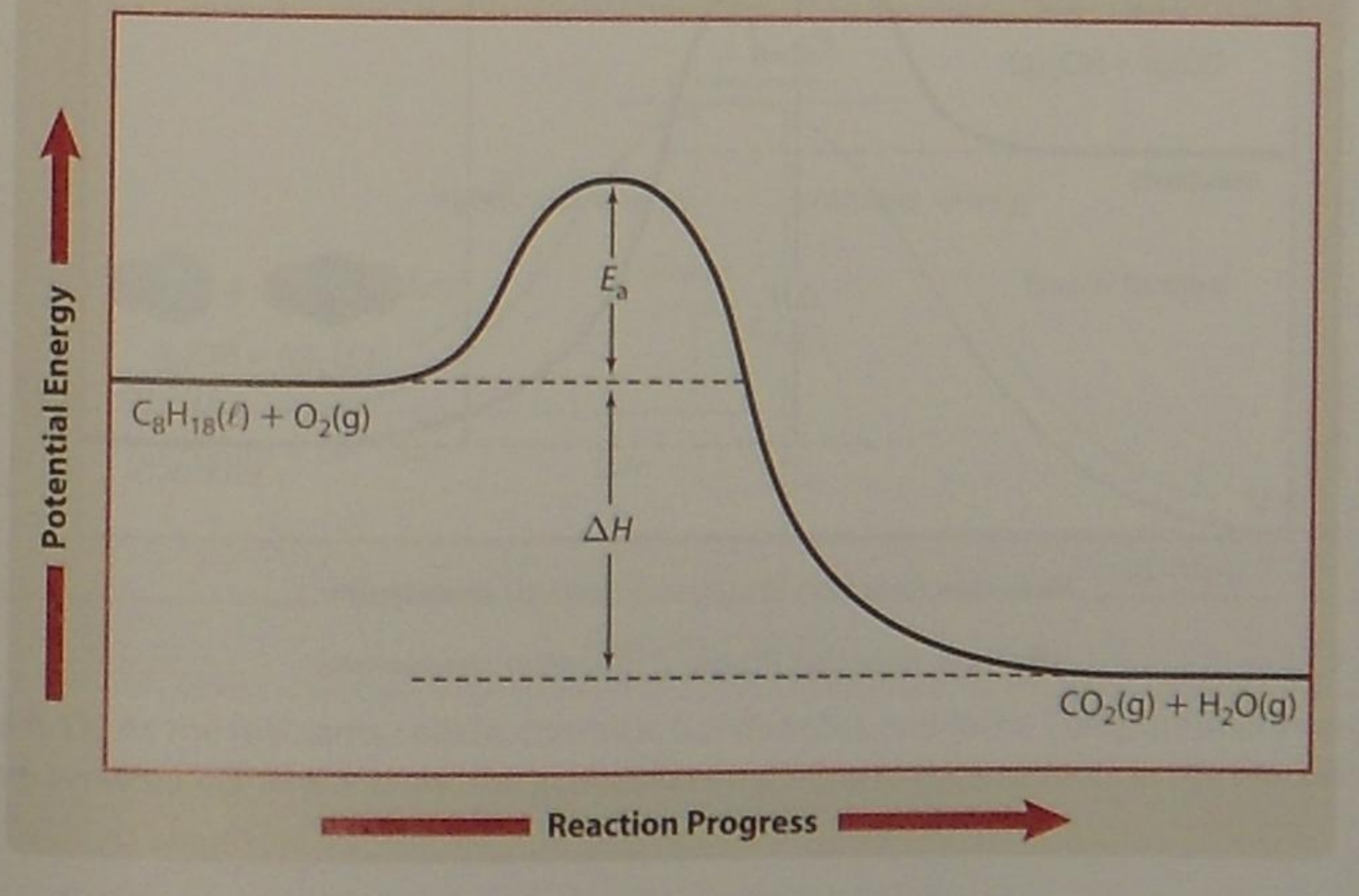


Figure 6.11 This potential energy diagram for the combustion of gasoline shows that gasoline does not burst into flame, because an activation energy is needed to initiate the reaction.

Activation Energy for Reversible Reactions

Many reactions can proceed in two directions: forward and reverse. For example, carbon monoxide and nitrogen dioxide react to form carbon dioxide and nitrogen monoxide, NO(g). This reaction, like many others, is reversible. Carbon dioxide and nitrogen monoxide can react to form carbon monoxide and nitrogen dioxide. The forward and reverse chemical equations are written below. Recall from Chapter 5 that when you write an equation with the ΔH_r notation, you must change the sign of ΔH_r for the equation of the reverse reaction.

Forward: $CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$ $\quad\Delta H_r = -226.1$ kJ

Reverse: $CO_2(g) + NO(g) \rightarrow CO(g) + NO_2(g)$ $\quad\Delta H_r = +226.1$ kJ

A potential energy diagram can represent the reaction in both the forward and reverse directions, as shown in **Figure 6.12**. To follow the forward reaction, go from left to right on the diagram. To follow the reverse reaction, go from right to left. Because the activation energies for the forward and reverse directions differ, add the subscript (fwd) to the activation energy for the forward direction: $E_{a(fwd)}$. Similarly, add the subscript (rev) to the activation energy for the reverse direction: $E_{a(rev)}$. Using this graph, you can see the relationships among the activation energies for the forward and reverse directions as well as the enthalpy change. The equation below also represents the relationship between these three terms.

$$E_{a(fwd)} - E_{a(rev)} = \Delta H_r$$

Thus, for exothermic reactions, ΔH_r is negative and the activation energy of the forward reaction is less than the activation energy for the reverse reaction. Conversely, for endothermic reactions, ΔH_r is positive and the activation energy of the forward reaction is larger than the activation energy of the reverse reaction.

Also included in **Figure 6.12** is the chemical species that exists at the top of the activation energy barrier, or in the transition state. It is referred to as an **activated complex**. An activated complex is neither a product nor a reactant. It is a temporary arrangement of atoms that form as bonds are breaking and new bonds are forming. Because the activated complex contains partial bonds, it is highly unstable. It can break down either to form products or to re-form reactants. The activated complex is like a rock teetering on top of a mountain. It could fall either way.

activated complex a chemical species temporarily formed by the colliding reactant molecules before the final product of the reaction is formed

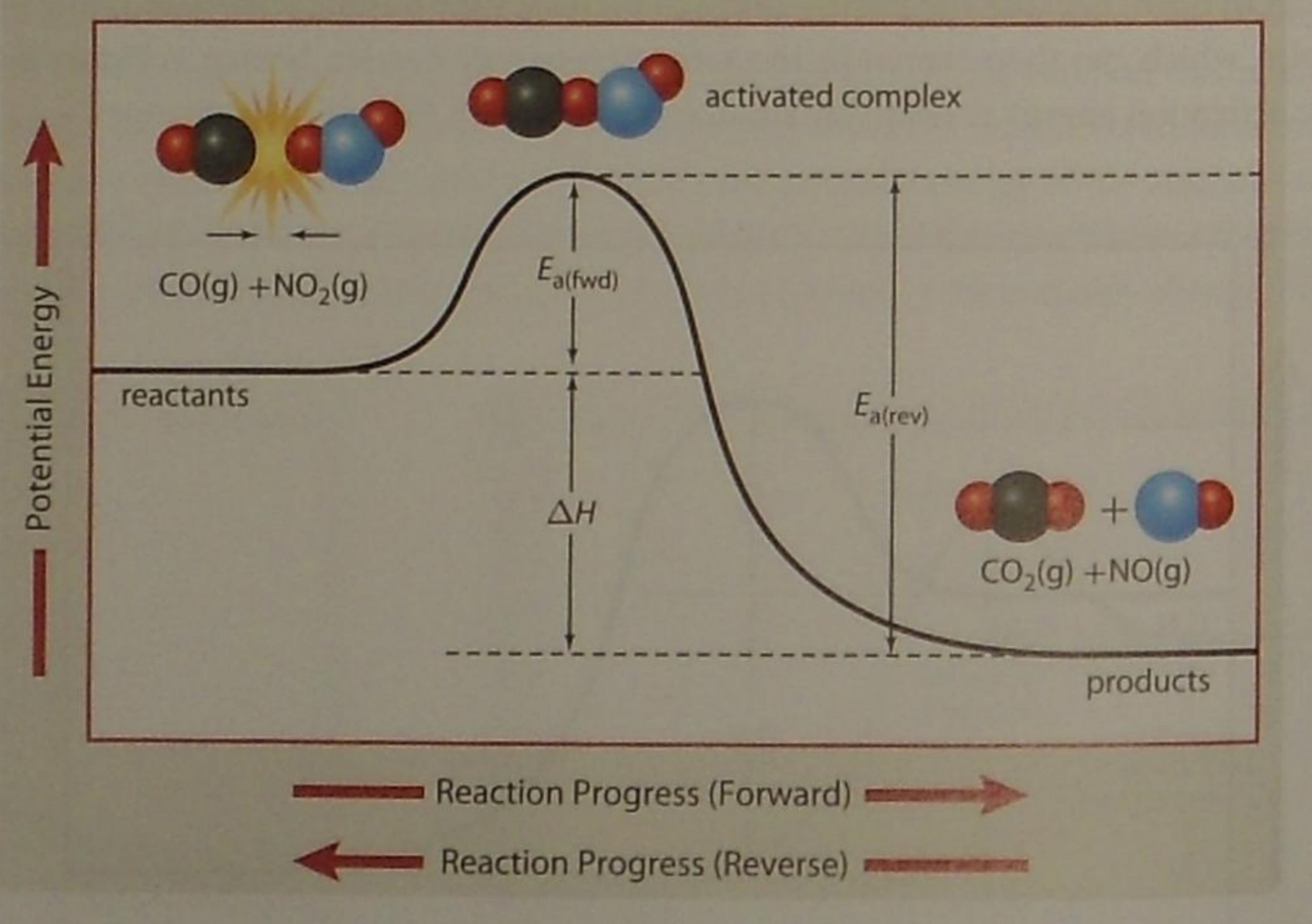


Figure 6.12 This potential energy diagram shows both a forward reaction between carbon monoxide and nitrogen dioxide and the reverse reaction between carbon dioxide and nitrogen monoxide. Atoms of the molecules shown are represented as follows: carbon is black, nitrogen is blue, and oxygen is red.

Learning Check

13. How does the magnitude of the activation energy generally affect the rate of a reaction?

14. Use collision theory to answer the following questions.

  a. Why is it necessary to use a lit match or other small flame to ignite a piece of paper?

  b. After lighting a barbecue that is fuelled by natural gas, the flame continues to burn on its own. Why is it not necessary to continually ignite the flame?

15. The enthalpy change for the conversion of graphite to diamond is +1.9 kJ/mol.

$$C_{graphite} + 1.9\text{ kJ} \rightarrow C_{diamond}$$

This small energy difference suggests this conversion is very simple. What information is not shown by the equation that would help explain why this conversion is not a simple process?

16. Answer the following questions about activated complexes.

  a. Explain what an activated complex is.

  b. Examine **Figure 6.8** and make a sketch of the activated complex for this reaction.

17. Given the data for a reaction, $E_{a(fwd)} = +45$ kJ, $E_{a(rev)} = +50$ kJ, is the reaction endothermic or exothermic? What is the magnitude of ΔH_r?

18. The decomposition of carbon disulfide, $CS_2(\ell)$, into its elements is represented by the equation shown below. Sketch the potential energy diagram corresponding to the *formation* equation for carbon disulfide.

$$CS_2(\ell) \rightarrow C(s) + 2S(s) + 89.0\text{ kJ}$$

Analyzing Reactions Using Potential Energy Diagrams

Consider the substitution reaction between a hydroxide ion and bromomethane:

$$BrCH_3(aq) + OH^-(aq) \rightarrow CH_3OH(aq) + Br^-(aq)$$

Figure 6.13 is a potential energy diagram that represents this reaction. It includes depictions at particular times of the reactants, the activated complex, and the products as the reaction proceeds.

For a reaction to take place, the bromomethane molecule and the hydroxide ion must collide. If the collision occurs at a favourable orientation with sufficient kinetic energy, the kinetic energy of the colliding particles is converted into potential energy. This potential energy is stored in the partial bonds of the activated complex, which is in transition between the reactants and the products. When the partial bonds of the activated complex re-form as chemical bonds, the potential energy that was stored is converted back into kinetic energy as the particles again separate. This conversion results in a decrease in potential energy with respect to the activated complex.

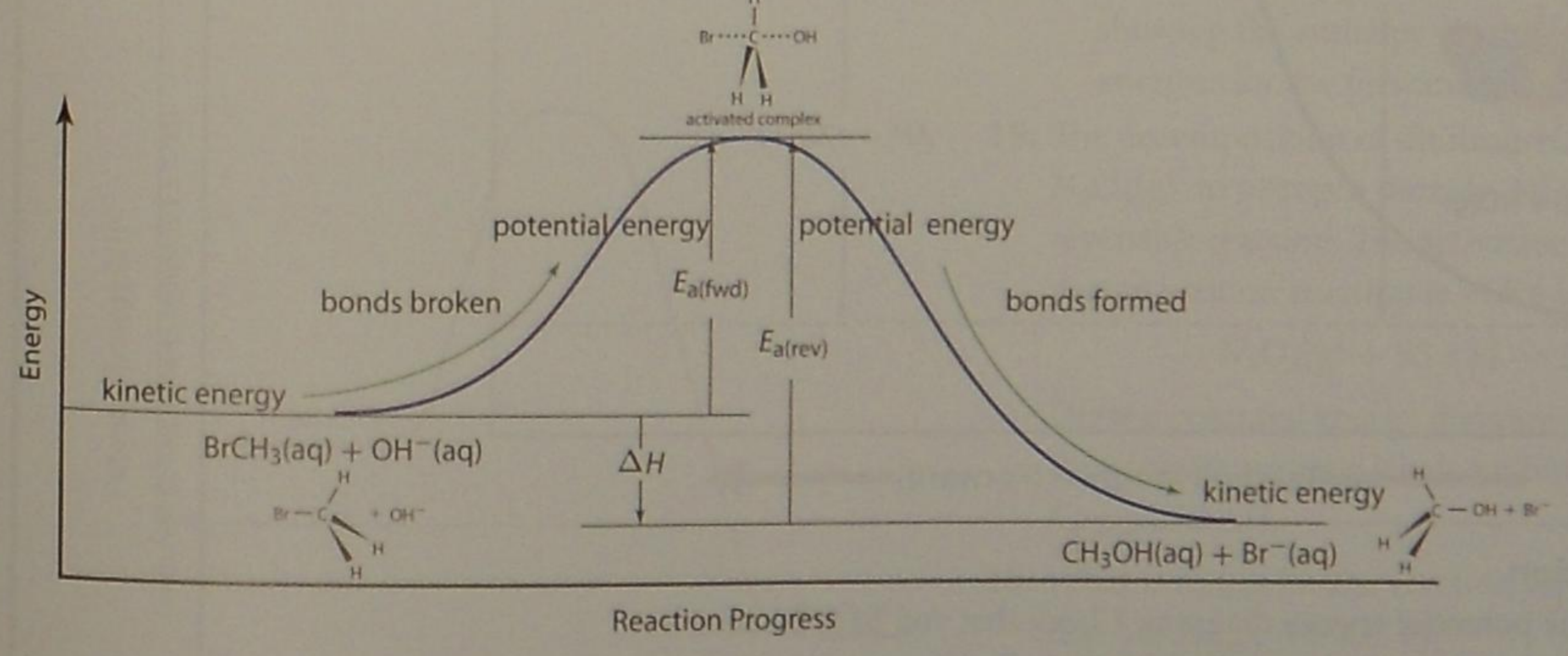


Figure 6.13 As the reactants collide, chemical bonds break and form. This potential energy diagram represents the reactants, the activated complex, and the products in the reaction.

Sample Problem

Representing a Reaction with a Potential Energy Diagram

Problem

Carbon dioxide, $CO_2(g)$, reacts with nitrogen monoxide, $NO(g)$. Carbon monoxide, $CO(g)$, and nitrogen dioxide, $NO_2(g)$, are formed. Draw a potential energy diagram to illustrate the progress of the reaction. (You do not need to draw your diagram to scale.) Label the axes, the transition state, and sketch and label the reactants, the products, and the activated complex. Indicate the activation energy of the forward reaction, $E_{a(fwd)} = +361$ kJ, as well as $\Delta H_r = +226$ kJ. Calculate the activation energy of the reverse reaction, $E_{a(rev)}$, and show it on the graph.

What Is Required?

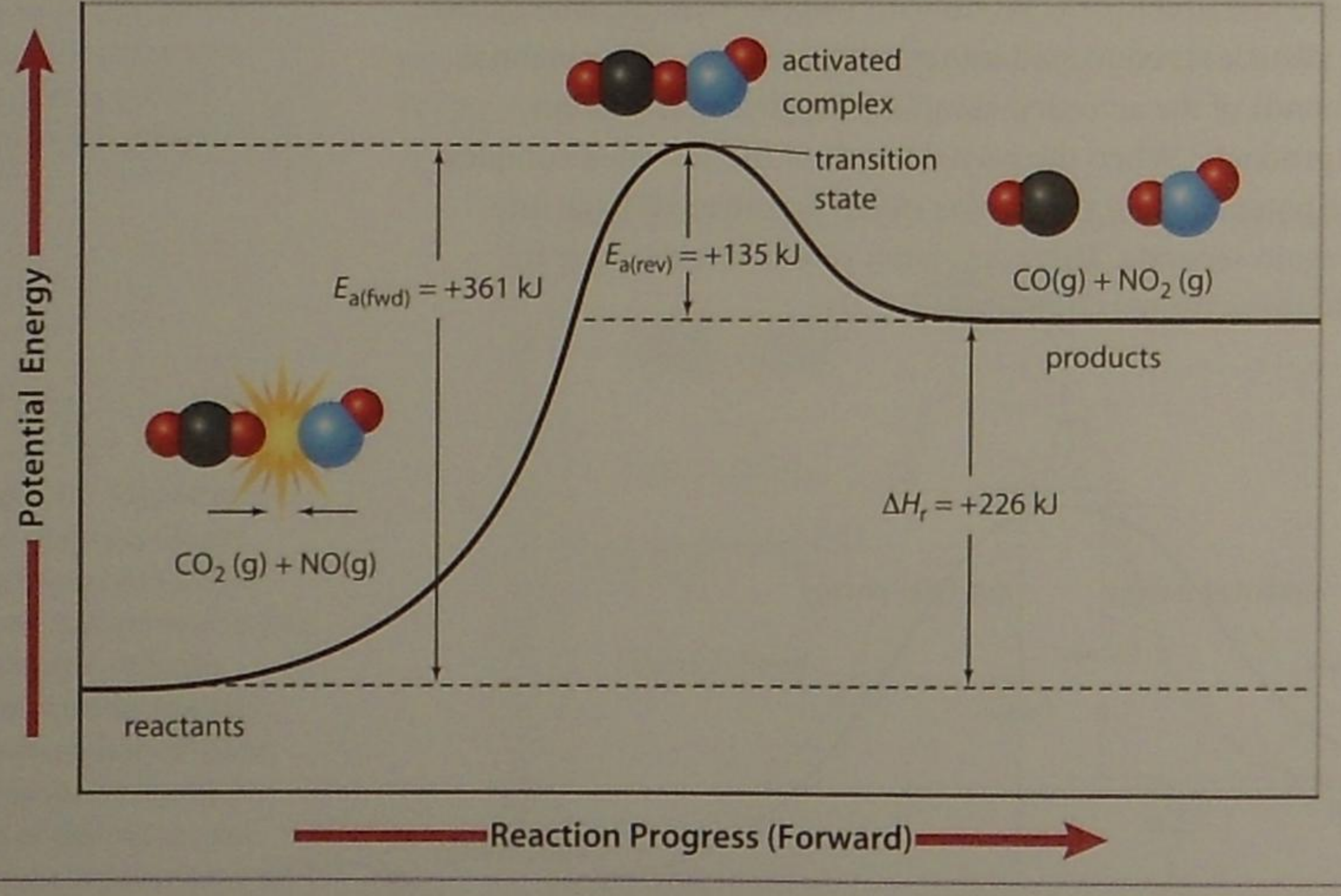
You need to draw a potential energy diagram for the reaction, labelling the x-axis and y-axis, and the transition state. You also need to include sketches and labels for the reactants, the products, and the activated complex, and indicate the activation energy and ΔH_r of the forward reaction. You then need to calculate the activation energy of the reverse reaction and show it on the graph.

What Is Given?

Activation energy of the forward reaction: $E_{a(fwd)} = +361$ kJ

Enthalpy change of the forward reaction: $\Delta H_r = +226$ kJ

Plan Your Strategy	Act on Your Strategy
Determine the activation energy of the reverse reaction using the formula $E_{a(fwd)} - E_{a(rev)} = \Delta H_r$.	$E_{a(rev)} = E_{a(fwd)} - \Delta H_r$ $= +361 \text{ kJ} - (+226 \text{ kJ})$ $= +135 \text{ kJ}$
Draw and label the potential energy diagram for the reaction.	



Check Your Solution

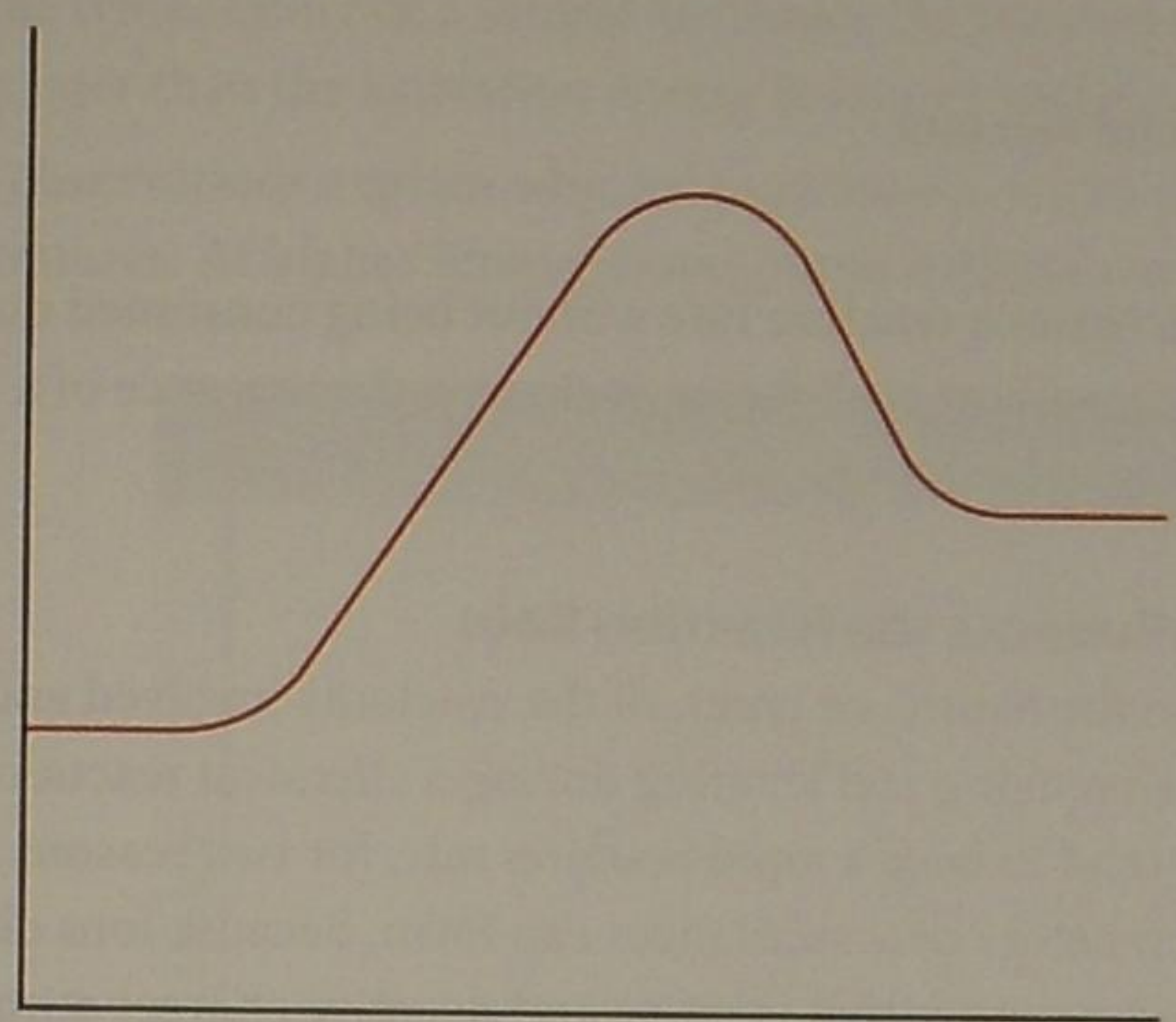
Look carefully at the potential energy diagram. Check that you have labelled it completely. Because the forward reaction is endothermic, the reactants should be shown at a lower energy level than the products, and they are. Using the potential energy diagram, you can confirm that the activation energy of the reverse reaction is +135 kJ.

Practice Problems

11. Complete the following potential energy diagram by adding the following labels: an appropriate label for the x-axis and y-axis, $E_{a(fwd)}$, $E_{a(rev)}$, ΔH_r.

a. Is the forward reaction endothermic or exothermic?

b. Which has the higher potential energy, the reactants or the products?



12. Consider the following reaction:

$AB + C \rightarrow AC + B \quad \Delta H_r = +65\ \text{kJ},\ E_{a(rev)} = +34\ \text{kJ}$

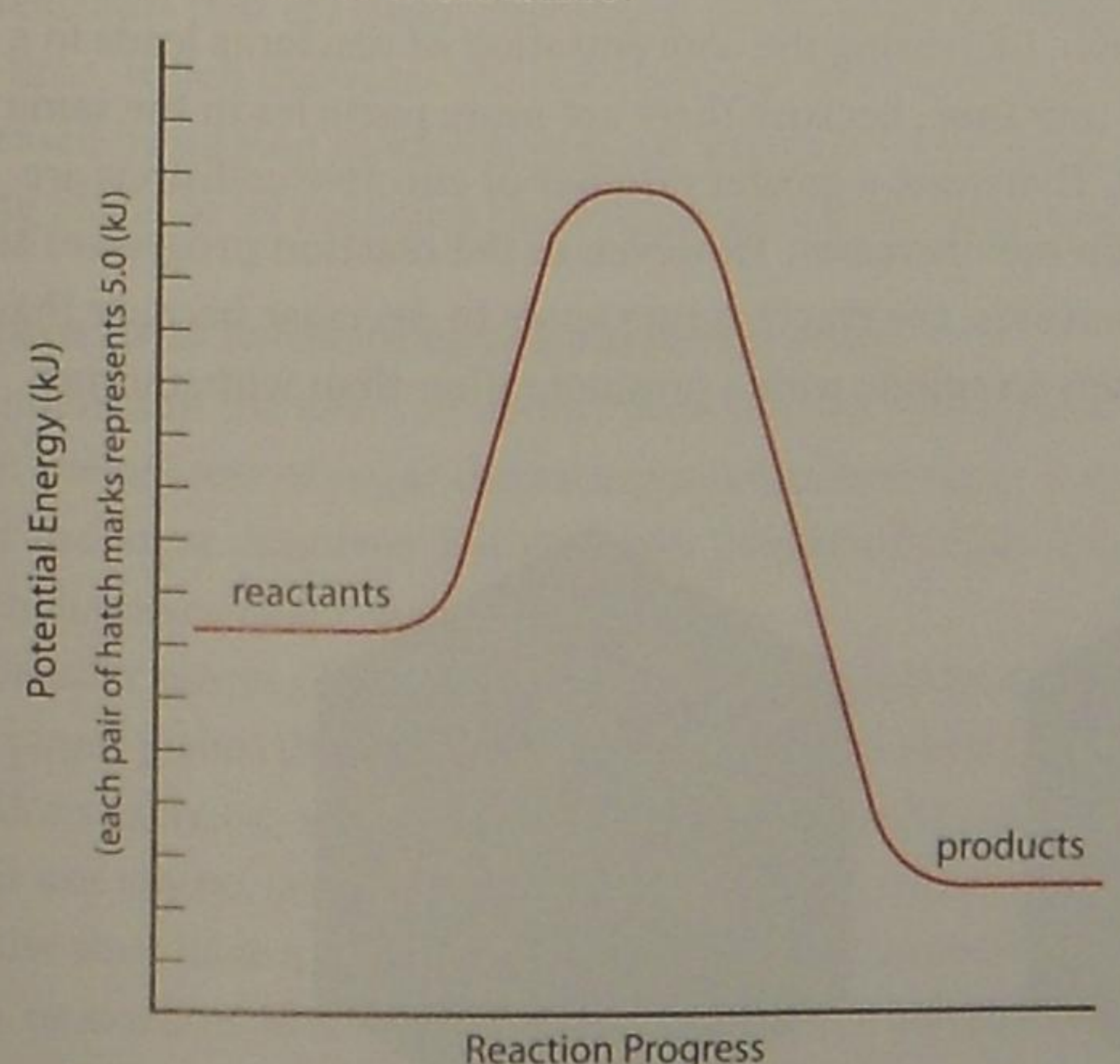
Draw and label a potential energy diagram for this reaction. Calculate and label $E_{a(fwd)}$.

13. Consider the reaction below:

$C + D \rightarrow CD \quad E_{a(fwd)} = +61\ \text{kJ},\ E_{a(rev)} = +150\ \text{kJ}$

Draw and label a potential energy diagram for this reaction. Calculate and label ΔH_r.

14. Using the potential energy diagram below, estimate the values for $E_{a(fwd)}$, $E_{a(rev)}$, and ΔH_r. Is the reaction endothermic or exothermic?



15. In the upper atmosphere, oxygen exists as $O_2(g)$, as ozone, $O_3(g)$, and as individual oxygen atoms, $O(g)$. Ozone and atomic oxygen react to form two molecules of oxygen gas. The enthalpy change is −392 kJ and the activation energy is +19.0 kJ. Draw and label a potential energy diagram. Include a value for $E_{a(rev)}$.

16. For a reaction, on an arbitrary scale, the potential energies are as follows: activated complex, +112 kJ; reactants, +36 kJ; products, +78 kJ.

a. Determine the activation energy and the enthalpy change for the reaction.

b. Draw a labelled potential energy diagram for the reaction, indicating the relative energies of the reactants, products, and activated complex.

17. Refer to the list of molar enthalpies of combustion for hydrocarbons in **Table 5.4**.

a. Write the balanced thermochemical equation for the combustion of methane gas, $CH_4(g)$.

b. Draw a potential energy diagram that would reasonably represent this combustion reaction. Indicate the ΔH_{comb} and a molecular structure that could represent an activated complex in this potential energy diagram.

18. When steam is passed over hot iron, a reaction occurs as shown below.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

$$\Delta H_r = -151.2\ \text{kJ}$$

The activation energy for the reverse reaction, $E_{a(rev)}$, is +200.71 kJ.

a. Calculate the activation energy for the forward reaction.

b. Draw a labelled potential energy diagram showing the enthalpy change, and the activation energies for the forward and reverse reactions.

19. The decomposition of dinitrogen tetroxide(g), $N_2O_4(g)$, to nitrogen dioxide, $NO_2(g)$, is a reversible reaction. The activation energy for the decomposition reaction is +58.6 kJ.

$$N_2O_4(g) + 55.3\ \text{kJ} \rightarrow 2NO_2(g)$$

Draw a potential energy diagram for the reaction showing appropriate labels for both axes, $E_{a(fwd)}$, $E_{a(rev)}$, and ΔH_r.

20. What is $E_{a(fwd)}$ for the reaction represented below that has $E_{a(rev)} = +235$ kJ?

$$A + 2CD + 85\ \text{kJ} \rightarrow G$$

Factors Affecting Reaction Rate

An understanding of collision theory contributes to an understanding of the factors that affect the rate at which a chemical reaction proceeds. In general, any factor that increases the frequency of collisions between particles also increases the rate of a chemical reaction, and any factor that decreases the frequency of collisions between particles also decreases the reaction rate. These factors include the following:

- nature of the reactants
- concentration of a solution
- temperature
- pressure of gases
- surface area of the particles of a solid reactant
- presence of a catalyst

catalyst a substance that increases the rate of a chemical reaction without being consumed by the reaction

A **catalyst** is a substance that increases a reaction rate without being consumed during the reaction. The following pages discuss how each factor, including the presence of a catalyst, can change the rate of a chemical reaction.

The Nature of the Reactants Influences the Reaction Rate

The reaction rate depends in part on the nature, or types, of the reactants involved and the types of chemical bonds that are breaking and forming during a chemical reaction. Reactions between ions in solution tend to have a rapid reaction rate, for two reasons. The first is that no bonds must be broken before new substances can form, because ions dissolve in water and move freely. The second reason is that positive and negative charges attract each other.

In general, like the reactions between ions, the reactions between acids and bases, which form salts, proceed rapidly because the acids and bases are often oppositely charged and thus attract each other.

Rates of reactions for molecules are usually slower than for ions. In molecular reactions, existing bonds must be broken before new bonds can form. During a particular chemical reaction, if the molecules of the reactants are large, must break apart, or have strong covalent bonds, then the reaction rate is generally slow. However, if the reaction is highly exothermic, like the reaction between octane and oxygen, and there is an external source of activation energy, then a few molecules will react. The energy released will give more reactant molecules enough kinetic energy to react, and the reaction will go to completion.

Concentration Influences the Reaction Rate

When a reaction occurs in solution, increasing the concentration of reactants leads to a greater number of collisions per unit time, because there are more particles in the same volume, as shown in **Figure 6.14**. Therefore, a greater number of effective collisions are likely to occur, and so the reaction rate increases. However, as the reaction progresses and the concentration of products increases, the reaction rate tends to decrease because the remaining reactants are more likely to collide with a product rather than with another reactant.

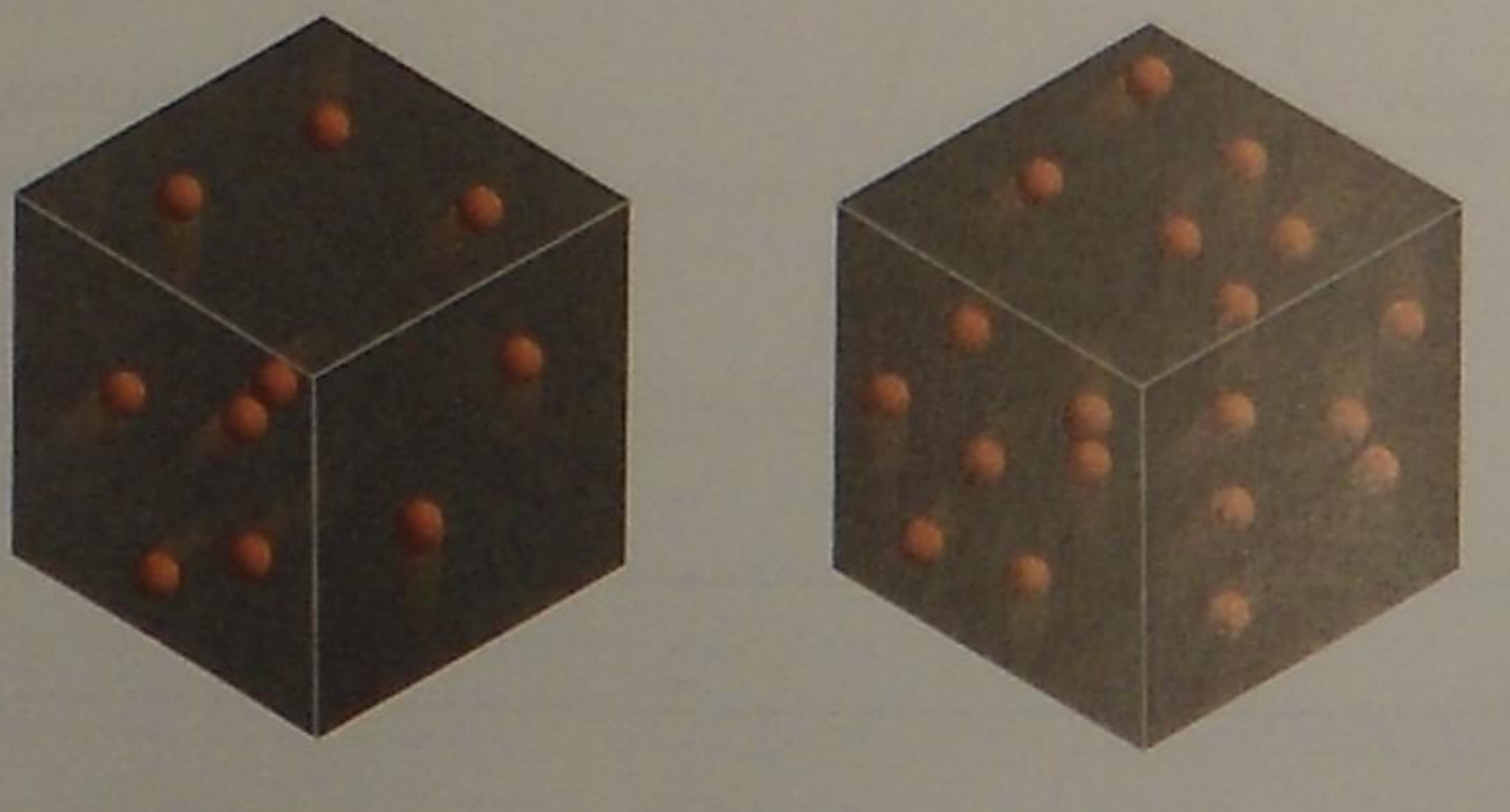


Figure 6.14 As the concentration of reactant particles increases, the rate of collision between the reactants also increases. Therefore, the rate of reaction increases.

Temperature Influences the Reaction Rate

The distribution of kinetic energy of the individual particles of a substance changes as the temperature of the substance changes. When temperature increases, particles have more kinetic energy. As a result, the frequency of collisions increases, and the number of effective collisions increases per unit of time. **Figure 6.15** shows the distribution of kinetic energy in a sample of reacting gases at two different temperatures, T_1 and T_2, where $T_2 > T_1$. The activation energy is indicated by the dashed vertical line. Two observations are apparent from the graph:

- At both temperatures, a relatively small fraction of collisions have enough energy for a collision to result in a reaction. ("Enough energy" means greater than or equal to activation energy.)
- As the temperature of a sample increases, the fraction of collisions with energy equal to or greater than the activation energy increases significantly.

These observations explain why, for most reactions, the reaction rate will increase at higher temperatures. At higher temperatures, more collisions are effective.

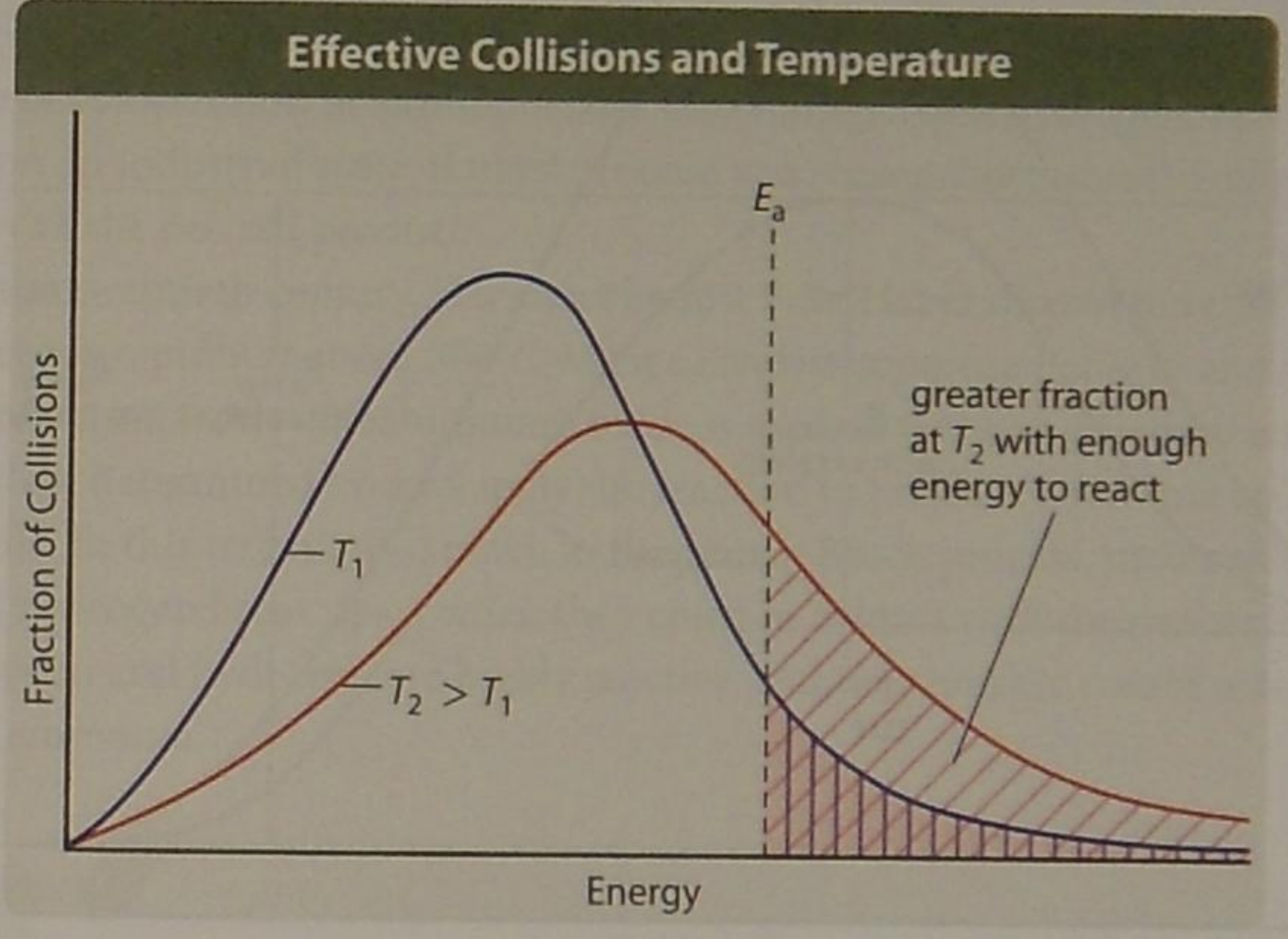


Figure 6.15 At increased temperatures, more particles collide with enough energy to react with one another. Therefore, increasing temperature speeds up the rate of a chemical reaction. ***Explain*** *how the relative number of collisions having sufficient activation energy is displayed for the two curves.*

Pressure Influences the Reaction Rate

For reactants that are gases, increasing the pressure increases the number of collisions per unit time, which increases the reaction rate. In accordance with Boyle's law, pressure can be increased by adding more reactant gas particles to the fixed volume in which a reaction is taking place, or by reducing the volume of the reaction container.

Surface Area Influences the Reaction Rate

To understand the effect of surface area of solid reactants on the rate of reaction, think about the process of sugar dissolving in a hot beverage. The greater the surface area, the faster the sugar dissolves. For example, powdered sugar dissolves faster than granular sugar, which dissolves faster than rock candy.

Smaller pieces of reactants have a greater amount of exposed surface area compared with larger pieces that have the same total mass. Therefore, the chances of effective collisions increase, and the rate of the reaction increases. However, this increase in reaction rate is not always desirable. Powdered materials, for example, are highly combustible, because they have a very large surface area. For example, coal dust in mines, flour dust in mills, or sawdust in a lumber mill can explode if a spark sets off a combustion reaction.

Suggested **Investigation**

Plan Your Own Investigation 6-A, Examining Reaction Rates

A Catalyst Influences the Reaction Rate

For some chemical reactions, the activation energy is so high that the reaction will either not occur at all or will occur very slowly, over days or even years. However, it is possible to increase the rate of a reaction by adding a particular substance known as a catalyst. A catalyst is a substance that increases the rate of a chemical reaction by lowering the activation energy. When the activation energy is lowered, a larger fraction of reactants have a kinetic energy equal to or greater than the activation energy. Speeding up reactions to make them practical and profitable for industrial applications is important, and it is often achieved by means of catalysts.

A *catalyzed reaction* is a reaction in which a catalyst has been used. The potential energy diagram in **Figure 6.16** compares the activation energy for an uncatalyzed reaction and the activation energy for the same reaction with the addition of a catalyst.

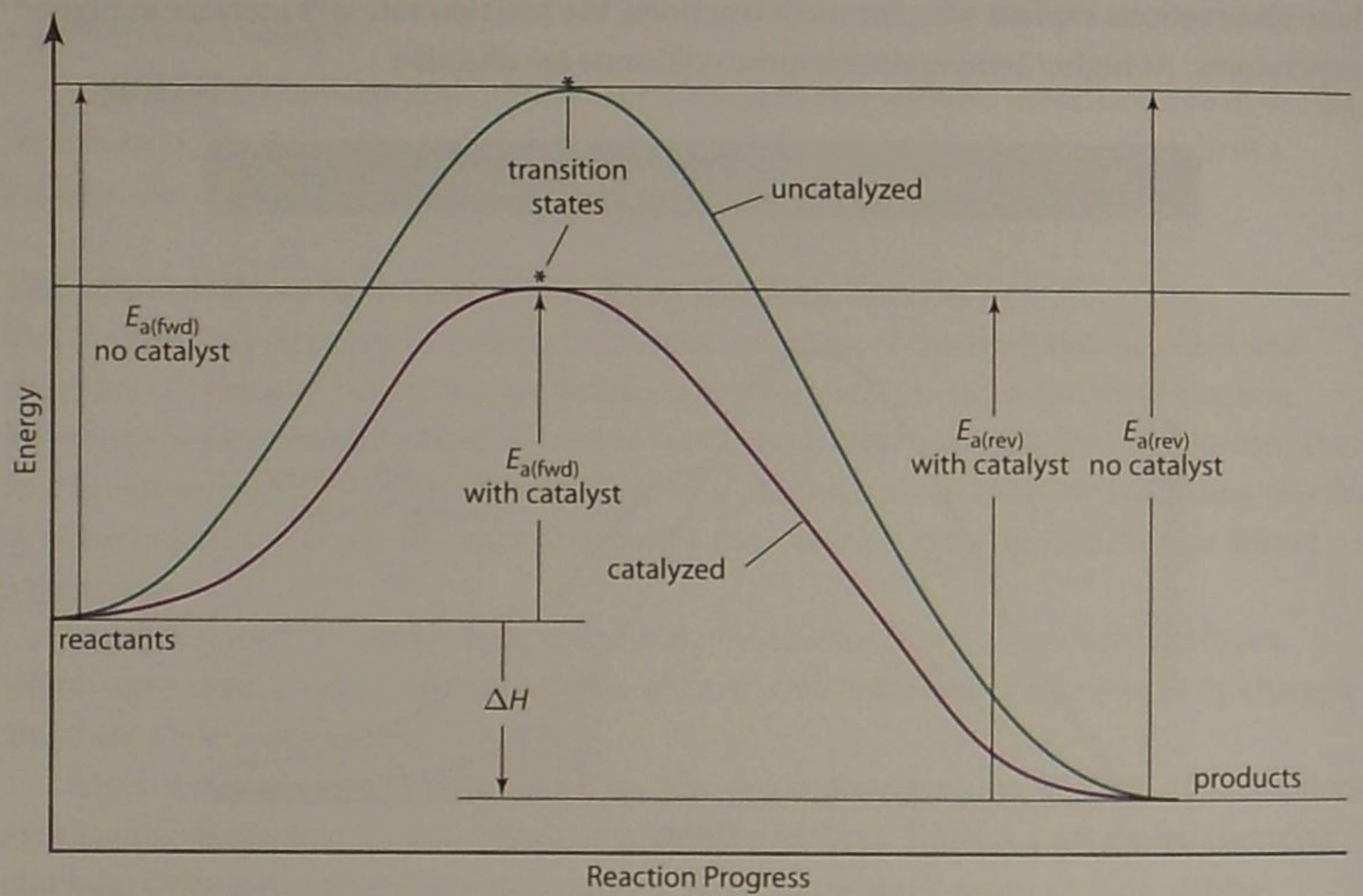


Figure 6.16 A catalyst causes the activation energy to be lower for a chemical reaction. A catalyst also increases the rate of the reverse reaction. ***Analyze*** *what effect a catalyst has on ΔH.*

Although the catalyzed reaction has the same reactants, products, and enthalpy change (ΔH) as the uncatalyzed reaction, the catalyzed reaction has a lower activation energy and therefore proceeds at a faster rate. The catalyst sometimes takes part in the reaction. However, even if the catalyst is changed during the reaction, it returns to its original condition by the time the overall reaction has reached completion.

Learning Check

19. How does collision theory explain a change in the rate of a chemical reaction?

20. Identify at least four factors that can alter the rate of a chemical reaction.

21. Use collision theory to explain the effect of a decrease in temperature on the reaction below:

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H_r = -283 \text{ kJ}$$

22. Iron, Fe(s), will rust as shown by the equation below:

$$Fe(s) + \frac{1}{2}O_2(g) + H_2O(\ell) \rightarrow Fe(OH)_2(s)$$

Using this equation and collision theory, explain how the rate at which rusting occurs could be slowed down.

23. Biomass fuels are now commonly manufactured as compressed pellets from waste products such as sawdust and plant material. In terms of collision theory, is there an advantage to burning this type of fuel as pellets rather than as sawdust or bulk plant material? Explain your answer.

24. The reaction $X(g) + Y(g) \rightarrow Z(s)$ occurs only at very high temperatures. Of the factors that affect the rate of reaction, which one would you expect to be the most effective in increasing the rate of the reaction? Explain your reasoning.

Catalysts in Industry

More than 3 000 000 t of catalysts are produced annually in North America. Newly discovered catalysts are patented by their manufacturers and kept as closely guarded secrets. Many reactions that produce useful compounds proceed too slowly to be used in industries. Some reactions need to be carried out at high temperatures or pressures to proceed quickly without a catalyst. These conditions, however, are expensive and dangerous to maintain. Therefore, when it is possible, chemists and engineers use catalysts to obtain products at a reasonable rate and under reasonable conditions.

The Production of Ammonia

Figure 6.17 illustrates the use of a catalyst to produce ammonia, $NH_3(g)$. Ammonia has numerous industrial applications, including the production of fertilizers and explosives. The formation of ammonia from nitrogen and hydrogen is exothermic, as shown below:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta H^\circ_r = -92.6 \text{ kJ/mol}$$

However, the reaction proceeds very slowly at room temperature. Increasing the temperature increases the reaction rate somewhat, but an increase in temperature also increases the decomposition of ammonia back into nitrogen and hydrogen. For the reaction to be useful on an industrial scale, it must proceed at a reasonably fast rate and generate a large quantity of the desired product.

Early in the twentieth century, German chemist Fritz Haber discovered that the reaction proceeds rapidly at about 500°C when a catalyst composed of iron and a small amount of potassium oxide and aluminum oxide is used. A German chemical engineer, Carl Bosch, then determined how to apply the reaction to produce ammonia on an industrial scale. In this technique, known as the Haber-Bosch process, molecules of nitrogen and hydrogen break apart when they come in contact with the metal catalyst. The atoms of nitrogen and hydrogen are highly reactive, and they quickly combine to produce molecules of ammonia.

Suggested Investigation

Plan Your Own Investigation 6-B, The Effect of a Catalyst on the Decomposition of $H_2O_2(aq)$

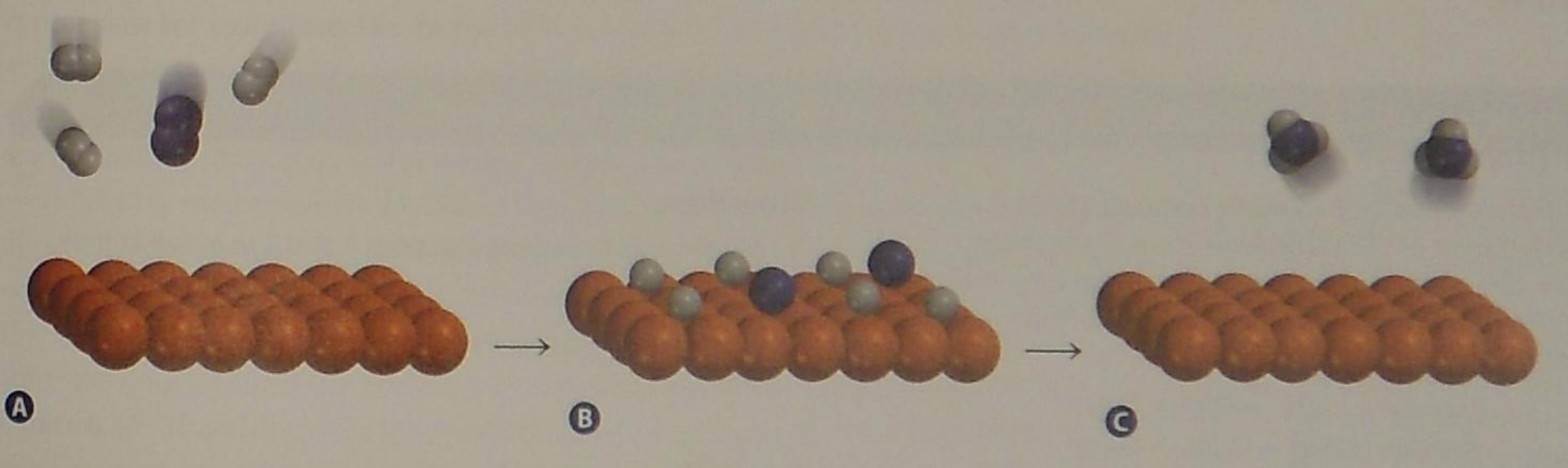


Figure 6.17 The synthesis of ammonia proceeds rapidly in the Haber-Bosch process as a result of the use of a catalyst.
Interpret *what is represented in parts A, B, and C of this diagram.*

The Production of Sulfuric Acid

Sulfur can be converted into sulfuric acid, an extremely important industrial acid used in such applications as manufacturing chemicals, refining ores, and processing waste water. The conversion process, called the *contact process*, uses vanadium(V) oxide, $V_2O_5(s)$, as a catalyst of one step in the process, as shown below. Without the catalyst, the reaction in step 2 would decrease the overall reaction rate. Notice that the catalyst is written above the reaction arrow, because it is not consumed during the reaction.

Step 1: $S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$

Step 2: $2SO_2(g) + O_2(g) \xrightarrow{V_2O_5(s)} 2SO_3(g)$

Step 3: $SO_3(g) + H_2SO_4(aq) \rightarrow H_2S_2O_7(aq)$

Step 4: $H_2S_2O_7(aq) + H_2O(\ell) \rightarrow 2H_2SO_4(aq)$

Suggested **Investigation**

ThoughtLab Investigation 6-C, Exploring Catalysts in Industry

The Production of Nitric Acid

Another important industrial acid, nitric acid, $HNO_3(aq)$, is produced using the Ostwald process. One major use of nitric acid is as a starting material for the production of ammonium nitrate, $NH_4NO_3(s)$, a fertilizer. The reaction steps of the Ostwald process are shown below. The first step is catalyzed using a platinum-rhodium catalyst (Pt-Rh) at 800°C. A photograph of the catalyst is shown in **Figure 6.18**. Notice that both nitric acid and nitrous acid are formed in step 3. When heated, nitrous acid is converted to nitric acid.

Step 1: $4NH_3(g) + 5O_2(g) \xrightarrow{\text{Pt-Rh,800°}} 4NO(g) + 6H_2O(g)$
Step 2: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
Step 3: $2NO_2(g) + H_2O(\ell) \rightarrow HNO_2(aq) + HNO_3(aq)$
Step 4: $3HNO_2(aq) \rightarrow HNO_3(aq) + H_2O(\ell) + 2NO(g)$

Figure 6.18 The platinum-rhodium catalyst, shown here, is in the form of a gauze or mesh to maximize its surface area.
***Explain** why it is important that the catalyst has a large surface area.*

The manufacture of catalysts for industrial applications has seen incredible growth in recent years because of environmental regulations surrounding acceptable levels of air pollution. In Ontario, the Ministry of the Environment has set regulations on industrial emissions of pollutants. These regulations have become more stringent and are being applied to more industries over time. Stricter standards applying to such facilities as petroleum refineries and iron and steel mills went into effect in 2010. As of 2013, application of these standards has extended to paper mills and factories that produce transportation equipment. All facilities must comply with the standards by 2020.

Catalysts are often used to convert pollutants in industrial emissions to less harmful forms. Regulated emissions include those of sulfur dioxide, $SO_2(g)$, and nitrogen oxides, $NO_x(g)$. A major source of both is the combustion of fossil fuels. The use of catalysts to convert sulfur dioxide into hydrogen sulfide, $H_2S(g)$, can reduce emissions of sulfur dioxide by up to 50 percent, and the use of catalysts to convert nitrogen oxides to nitrogen gas and water can reduce emissions of nitrogen oxides by up to 95 percent.

Activity 6.2 Chlorofluorocarbons as Catalysts in Ozone Depletion

In the absence of human-made compounds, the concentration of UV-absorbing ozone, $O_3(g)$, in the stratosphere is constant. That is, its rates of formation and decomposition are equal. A simplified explanation for ozone formation is given as follows:

Reaction 1: $O_2(g) \xrightarrow{UV} O(g) + O(g)$
Reaction 2: $O(g) + O_2(g) \rightarrow O_3(g)$

In addition, ozone can decompose upon absorbing UV light:

Reaction 3: $O_3(g) \xrightarrow{UV} O_2(g) + O(g)$

The introduction of chlorofluorocarbons ($C_xCl_yF_z$) into the atmosphere has affected the balance of ozone formation and decomposition. Once these CFCs diffuse into the stratosphere, they decompose in the presence of UV radiation:

Reaction 4: $CF_2Cl_2(g) \xrightarrow{UV} CF_2Cl\cdot(g) + Cl\cdot(g)$

The reactive chlorine atoms (Cl·) produced in reaction 4 are called chloride radicals. All radicals are highly reactive and react with ozone in the following two-step process:

Reaction 5: $Cl\cdot(g) + O_3(g) \rightarrow ClO\cdot(g) + O_2(g)$
Reaction 6: $ClO\cdot(g) + O(g) \rightarrow Cl\cdot(g) + O_2(g)$

Procedure

1. Algebraically combine reactions 1 and 2 to arrive at their sum.
2. Algebraically combine reactions 5 and 6 to arrive at their sum.

Questions

1. What does the sum of reactions 1 and 2 represent?
2. How does the rate of the overall reaction from question 1 compare with the rate of reaction 3?
3. What causes the reaction represented by reaction 4?
4. What does the sum of reactions 5 and 6 represent?
5. Does Cl·(g) appear in the sum of reactions 5 and 6? Explain why Cl·(g) is a catalyst in the overall reaction.
6. Does ClO·(g) appear in the overall equation? Explain why ClO·(g) is *not* a catalyst in this reaction; explain its role in the reaction.
7. Discuss the overall effect of the presence of CFCs in the upper atmosphere.

Learning Check

25. How can the use of a catalyst in an industrial process be an advantage for a company?
26. What property of a substance is most important in determining if it will be suitable for use as a catalyst in an industrial process?
27. In the contact process for producing sulfuric acid, the catalyst vanadium(V) oxide, $V_2O_5(s)$, will increase the rates of the forward and reverse reactions for the following system:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + \text{heat}$$

   a. Draw a labelled potential energy diagram that could represent this process.
   b. Use collision theory to explain why the rates of the forward and the reverse reactions increase when the catalyst vanadium(V) oxide is present.
   c. How does the catalyst affect ΔH_{fwd} and ΔH_{rev}?
28. What industries are most affected by stricter government emission standards? What is the reason that these industries are targeted for strict emission controls?
29. In the Haber-Bosch process, ammonia gas, $NH_3(g)$, is produced in a catalyzed, exothermic reaction at a high temperature.
   a. Write the balanced thermochemical equation for the formation of ammonia from its elements.
   b. Why is a very high temperature used for the reaction? What problem is caused by the use of a higher temperature?
   c. What catalyst is used in this process? How does it increase the rate of reaction?
30. Explain how Haber and Bosch separately contributed to the development of the process that bears their names. Why is it important for industries to have teams of people solving problems and developing new catalysts instead of individual scientists working alone?

The Use of Biological Catalysts (Enzymes) in Paper Production

enzyme a biological catalyst (usually a protein)

In industrial applications, as you have learned, chemists often use an increase in temperature to increase the rate of a chemical reaction, with or without a catalyst. In a living organism, however, all chemical reactions must proceed under conditions appropriate for sustaining life. In the human body, for example, reactions must take place at body temperature, 37°C. Living organisms depend on reactions that are catalyzed by amazingly efficient biological catalysts called **enzymes**. Enzymes are usually proteins that are specialized to catalyze only one or a few specific reactions.

Many types of enzymes are used in industrial processes. Consider the manufacture of paper, which is made by separating plant fibres from other plant material and then compressing the moist fibres into thin sheets and drying them. A substance called xylan that is present in plant fibres makes it more difficult to remove the natural brown colour from the fibres. Unless the fibres are bleached, paper will be brown, as shown in **Figure 6.19**. Therefore, chlorine-based bleaches, which can be damaging to the environment, are often used in the production of white paper. However, a class of enzymes called xylanases break down xylan. Xylanases are naturally produced by organisms such as fungi and some bacteria that can degrade the cell walls of plants. During paper production, the addition of xylanases allows for much smaller concentrations of bleach to be used to produce white paper. The waste water that is released into the environment from paper manufacturing plants therefore contains reduced concentrations of bleach. Besides lessening the environmental impact, the use of biocatalysts in producing paper also means that fewer chemicals are needed in the process and less energy is consumed in the process as well.

Another type of enzyme used to produce paper is called amylase. This enzyme is used in the production of the starch that can be added to paper. The starch improves the strength of the paper and increases its ability to withstand the friction of erasers.

Figure 6.19 Unbleached paper is naturally light tan to brown in colour, depending on the types of fibres used to make the paper. To manufacture white paper, the colour of the fibres must be removed. The use of enzymes can greatly reduce the amount of bleach needed to decolourize plant fibres.

CHEMISTRY Connections

Inside a Catalytic Converter: Car Pollution Solution?

Since the introduction of catalytic converters in 1975, they have become mandatory for all new vehicles. When car engines burn fuel, they produce exhaust, made up primarily of nitrogen gas, carbon dioxide gas, and water vapour. Although carbon dioxide is a greenhouse gas that contributes to global warming, it is not the most harmful emission. Because combustion in an engine is not complete, car engines also produce smaller amounts of the poisonous gas carbon monoxide, $CO(g)$, as well as hydrocarbons and nitrogen oxides, $NO(g)$ and $NO_2(g)$. Each of these substances contributes to the formation of smog and acid precipitation.

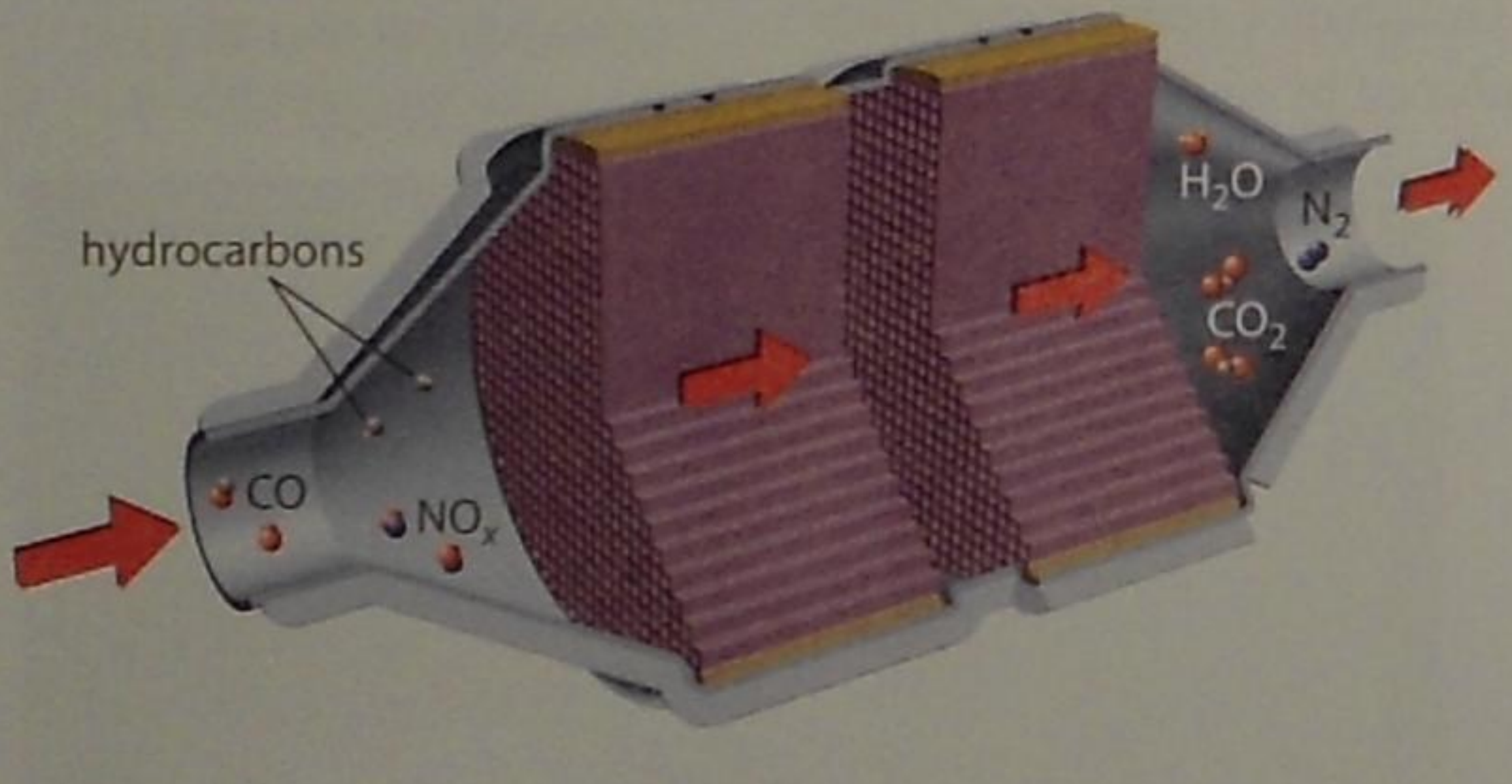
Three Stages of Conversion

Most modern vehicles are equipped with a three-way catalytic converter that is located in the exhaust system and exposed to the exhaust stream. Most three-way catalytic converters consist of a honeycomb-shaped structure, shown in the illustration below, coated with the metal catalysts platinum, palladium, and rhodium. As engine exhaust gases flow through the exhaust pipe into the honeycomb passageways of the catalytic converter, they come into contact with the metal catalysts, as shown in the illustration below.

Three-way catalytic converters reduce emissions of carbon monoxide, hydrocarbons, and nitrogen oxides in three stages:

Stage 1: The platinum and rhodium catalyze reactions that convert nitrogen oxides and carbon monoxide into nitrogen gas and carbon dioxide.

$$2NO(g) \xrightarrow{Pt(s),Rh(s)} O_2(g) + N_2(g)$$
$$2NO_2(g) \xrightarrow{Pt(s),Rh(s)} 2O_2(g) + N_2(g)$$



Chemical reactions occurring in a three-way catalytic converter change carbon monoxide to carbon dioxide, nitrogen oxides to nitrogen gas, and hydrocarbons to water vapour and carbon dioxide. As a result, the emission of pollutants is greatly reduced.

Stage 2: The platinum and palladium catalyze the complete combustion of the hydrocarbons and carbon monoxide, producing water vapour and carbon dioxide.

$$C_xH_y(g) + O_2(g) \xrightarrow{Pt(s),Pd(s)} CO_2(g) + H_2O(g)$$
$$2CO(g) + O_2(g) \xrightarrow{Pt(s),Pd(s)} 2CO_2(g)$$

Stage 3: For complete combustion to take place, the correct concentration of oxygen must be present in the exhaust. During the third stage, an oxygen sensor mounted between the car's engine and the three-way catalytic converter determines the amount of oxygen that there is in the exhaust and relays this information to the engine computer. The engine computer can control the amount of oxygen in the exhaust by adjusting the air-to-fuel ratio.

An Imperfect Solution

The catalytic converter can eliminate up to 95 percent of hydrocarbons, carbon monoxide, and nitrogen oxides, but it is not perfect. The exhaust still contains carbon dioxide, which contributes to global warming. Moreover, the three-way catalytic converter only begins to work at a relatively high temperature. It begins to operate at around 288°C, and efficient conversion starts at 399°C. Thus, when you start your car on a cold day, harmful gases escape with the exhaust until the catalytic converter heats up. Using a block heater in vehicles during the colder months of the year helps to combat this problem.

Connect to Technology

1. Research the environmental effects of the chemicals that are emitted in vehicle exhaust.
   a. What level of risk from the emission of these chemicals do you think is acceptable? Use a risk-benefit analysis chart to support your answer.
   b. Research which level of government regulates vehicle emissions in Ontario and what it is doing to reduce vehicle emissions.
2. Catalytic converters can produce dinitrogen monoxide, $N_2O(g)$, commonly known as "laughing gas," which makes up about 7.2 percent of greenhouse gases. Although the industry proposes re-designing the catalytic converter, environmentalists argue that this is another reason to move away from gasoline-powered cars to electric or hybrid cars. Which do you think is the better solution to the problem? Give research-based reasons to support your answer.

Section 6.2 Review

Section Summary

- According to collision theory, a reaction will occur only if the reactants collide with the correct orientation and with energy equal to or greater than the activation energy, E_a.
- When reactants collide with sufficient energy to overcome the activation energy barrier, they form an activated complex, which is an unstable transition state.
- A potential energy diagram can represent reversible reactions. For the reverse reaction, follow the curve from right to left.
- Factors that affect the rate of a chemical reaction include the nature of the reactants, the concentration of a solution, temperature, the pressure of gaseous reactants, the surface area of solid particles of the reactants, and the presence of a catalyst.
- A catalyst is a substance that increases the rate of a reaction but is itself unchanged at the end of the reaction.
- Biological catalysts are called enzymes and are specialized to catalyze only one or a few specific reactions. Enzymes can be used in industrial applications to reduce the use of chemicals that can adversely affect the environment.

Review Questions

1. **K/U** Describe the energy conversions that take place during a chemical reaction. Use the terms *kinetic energy*, *potential energy*, *bonds breaking*, and *bonds forming* in your answer.
2. **K/U** What information can be obtained from a potential energy diagram?
3. **K/U** What criteria must be met to create an effective collision between reactant particles?
4. **K/U** Is the activated complex a reactant or a product in a reaction? Explain your answer.
5. **T/I** An activated complex has been compared to a boulder sitting on the peak of a mountain. Explain why this is an appropriate comparison.
6. **T/I** A forward reaction has an activation energy of +45 kJ and an enthalpy change of –45 kJ. Sketch a potential energy diagram for the reaction. Label $E_{a(fwd)}$, $E_{a(rev)}$, and ΔH_r.
7. **C** Using collision theory and diagrams, explain to a friend how surface area can affect the rate of a reaction.
8. **C** Your lab partner argues that it is not possible for reactions that have a high activation energy to have a rapid rate of reaction. What example of a reaction could you give to dispute this argument? Explain your answer.
9. **T/I** You are designing an experiment to determine the effect of concentration on the rate of the reaction between hydrochloric acid and marble chips by measuring the volume of carbon dioxide gas produced over a period of time.

   $$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(\ell) + CO_2(g)$$

   As the concentration of acid is changed for several trials, what factors would you control in each trial to ensure that the acid concentration is the only factor affecting the reaction rate?
10. **A** A company is looking for the optimum conditions to produce hydrogen gas using the reaction between dilute sulfuric acid and magnesium metal. Predict whether the rate of reaction will increase, decrease, or remain the same when each one of the following changes is made. Support your answer with reference to collision theory.

    $$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

    a. The temperature of $H_2SO_4(aq)$ is decreased by 20°C.
    b. Magnesium powder is used rather than the equivalent mass of cubes of metal.
    c. The reaction is carried out in a closed vessel in which the pressure is increased.
    d. The concentration of $H_2SO_4(aq)$ is increased from 3 mol/L to 6 mol/L.
11. **T/I** A catalyst has been found to lower the activation energy of an exothermic reaction in the forward direction by 50 percent. Use this information with the data below to calculate the enthalpy change of the forward reaction. Sketch your results using a reasonable scale in a potential energy diagram.

    $E_{a(fwd)} = +160$ kJ (uncatalyzed)
    $E_{a(rev)} = +240$ kJ (catalyzed)
12. **C** Consider the following reaction:

    $A_2(g) + B_2(g) \rightarrow 2AB(g)$
    $E_{a(fwd)} = +143$ kJ
    $E_{a(rev)} = +75$ kJ

    a. Is the reaction endothermic or exothermic in the forward direction?
    b. Draw and label a potential energy diagram for this reaction. Include a value for ΔH_r.

SECTION 6.3 Reaction Rates and Reaction Mechanisms

Key Terms

initial rate
reaction mechanism
elementary step
intermediate
rate-determining step

As you know from Section 6.2, the rate of a reaction depends in part on the concentration of the reactants. When the concentration of reactants increases, the reaction rate tends to increase, because a greater number of collisions occur per unit time within the same volume. The increase in the number of collisions increases opportunities for effective collisions to take place. In this section, you will look more closely at the effect of concentration of reactants and products on rates of reactions in order to develop an understanding of reaction mechanisms—the detailed steps that occur during reactions.

Measuring the Effect of Concentration on Reaction Rate

Several concepts from Section 6.1 are reviewed in **Figure 6.20**, which shows three examples of lines tangent to the curve, with triangles formed from the slopes. The slopes are equal to $\frac{\Delta[A]}{\Delta t}$ at one instant in time. The slopes of these tangents therefore represent the instantaneous rate of the reaction for those instants in time. As time progresses, the slopes become smaller, because the concentration is decreasing. Therefore, the reaction rates become smaller.

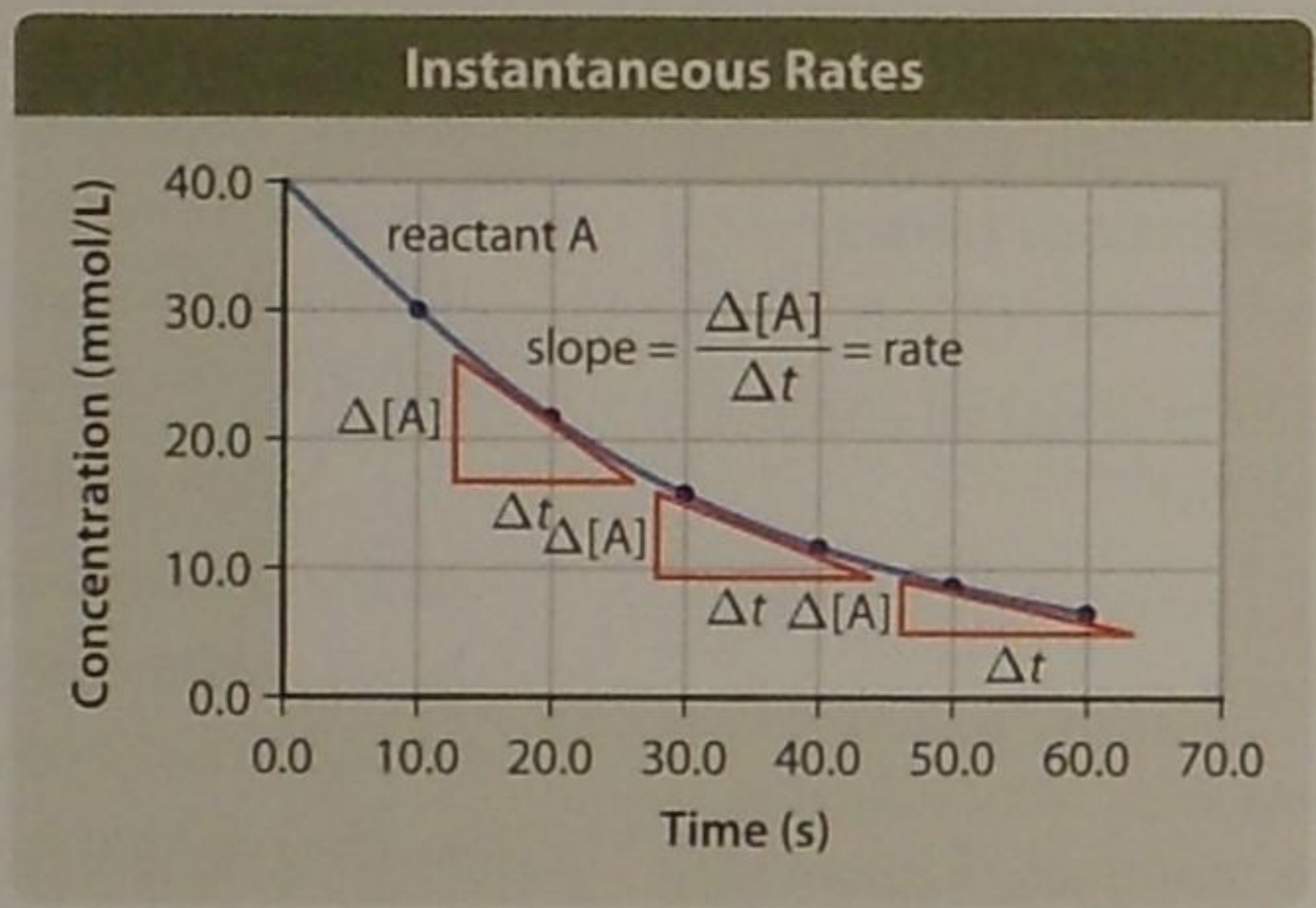


Figure 6.20 To find the instantaneous rate of a reaction at any point in time, draw a line tangent to the curve at that time point and calculate the slope of the tangent.

As soon as a reaction starts, products begin to form. The presence of products allows reverse reactions to take place. Thus, the observed rate of a reaction, measured at any time after time zero, is affected by the rate of the reverse reaction. The only accurate datum for the relationship between the concentration of a reactant and the reaction rate is the point at which there is no product present—at time zero. This point is called the **initial rate**, and can be determined by drawing a line tangent to the curve at time zero, as shown in **Figure 6.21**.

initial rate the rate of a chemical reaction at time zero

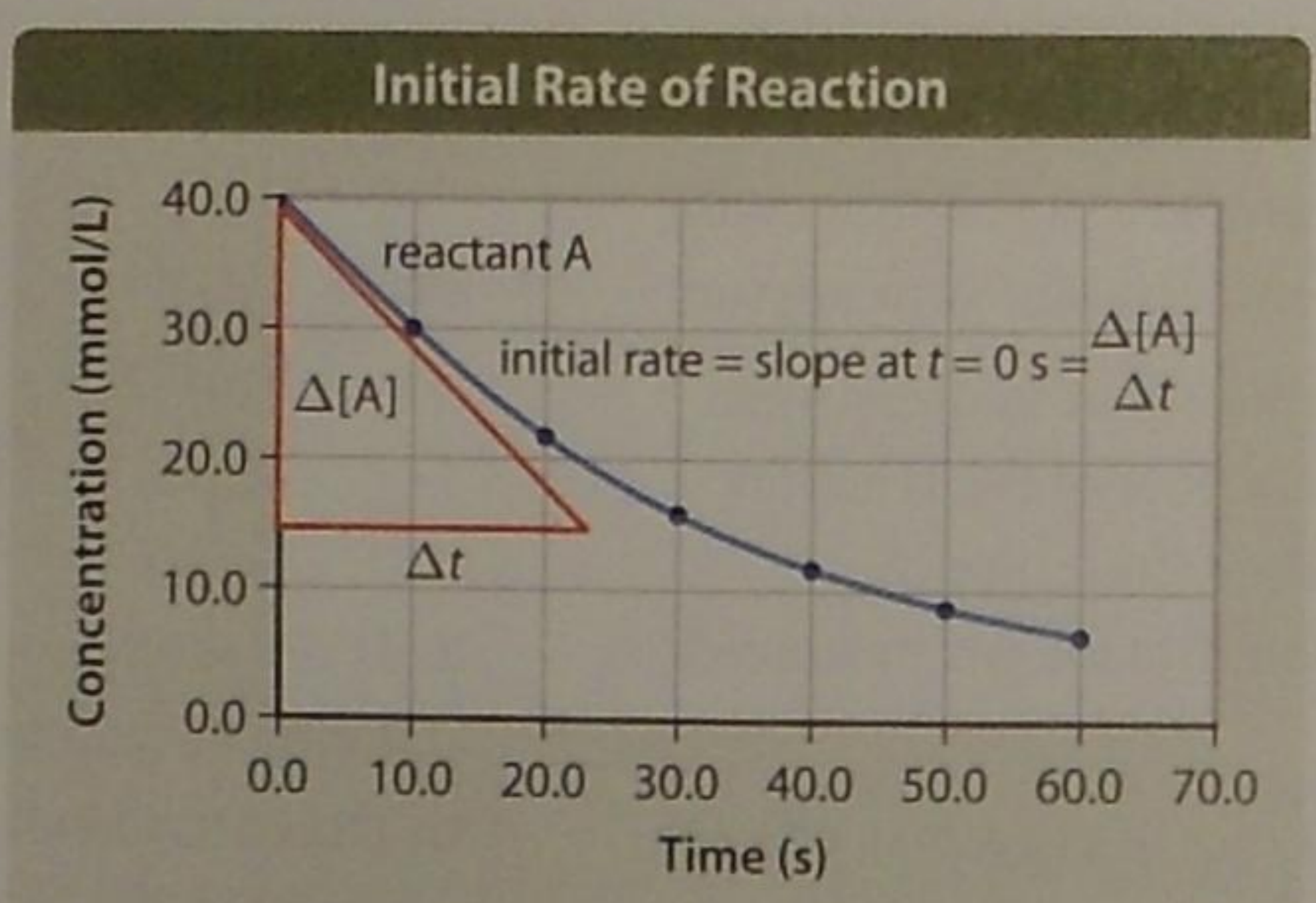


Figure 6.21 The initial rate of a reaction is found by drawing a line tangent to the curve at time zero and determining the slope of the line. Thus, the instantaneous rate of a reaction at $t = 0$ s is the initial rate of the reaction.

Graphing Reaction Rate in Terms of Concentration

To observe the effects of concentration on the rate of a reaction, several experiments are carried out, each one starting with a different concentration of reactant. Graphs are drawn and the initial rate for each curve is determined, as shown in **Figure 6.22A**. Each of the five curves represents data from a different experiment, and each experiment uses a different starting concentration of the reactant. **Figure 6.22B** is a graph of the initial rates determined from graph A and plotted against the starting concentrations of each of the experiments.

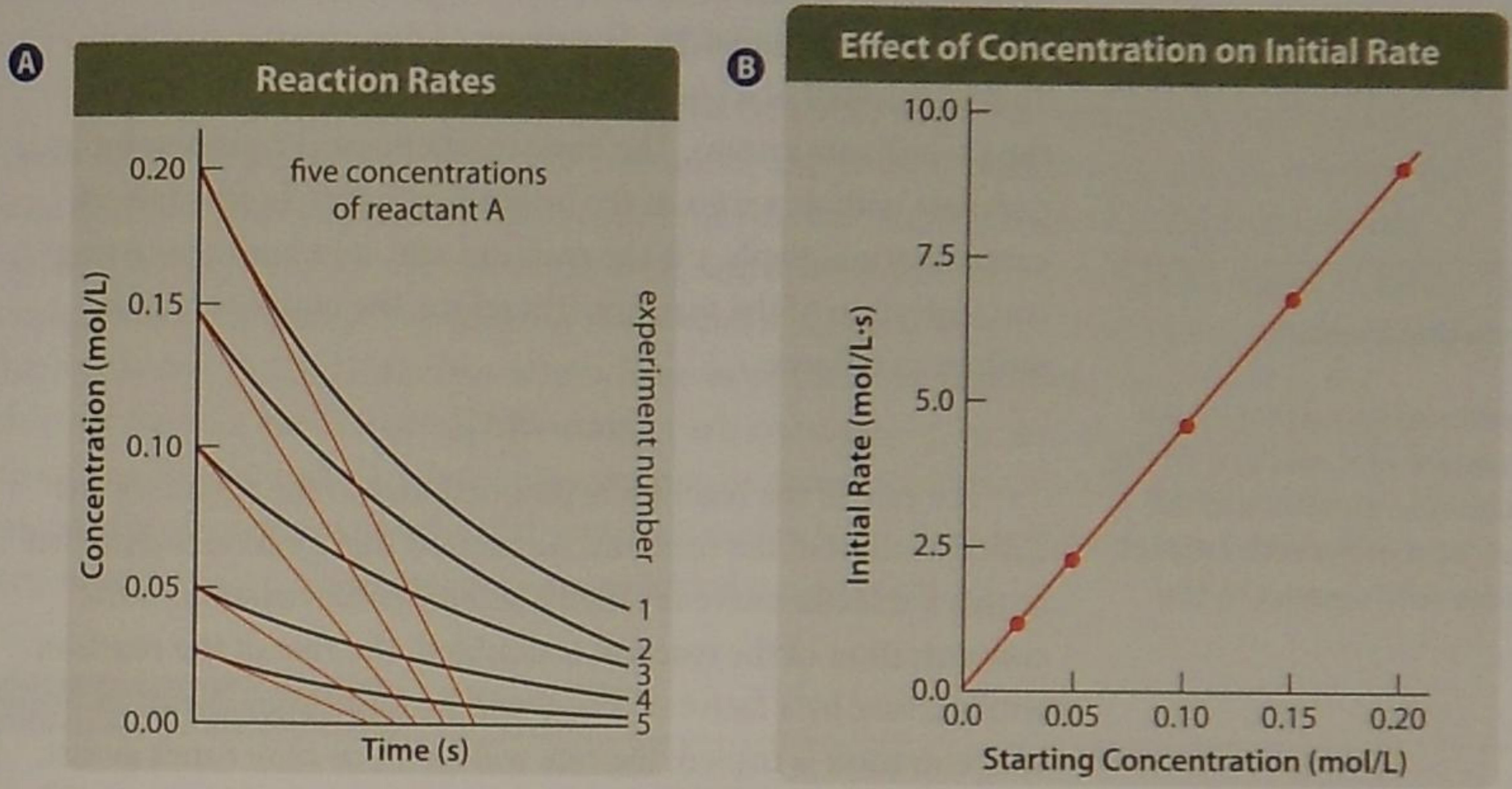


Figure 6.22 In graph **(A)**, rate curves for five concentrations of reactant A are plotted and the initial rates are calculated. In graph **(B)**, the initial rates for each concentration are plotted against the starting concentration.

The graph in **Figure 6.22B** shows that, in this case, the relationship between the initial rate of the reaction and the starting concentration of reactant A is a straight-line plot. Recall that the general equation for a straight line is $y = mx + b$. In **Figure 6.22B**, y is the initial rate of the reaction, x is the starting concentration, and m is the slope. The constant b is the point at which the line crosses the y-axis, which is zero in this case. Therefore, the results can be expressed mathematically: initial rate $= m[\mathrm{A}]$. In chemistry, the slope of this line is usually represented by the symbol k, and the initial rate is usually simply called the rate. Therefore, this relationship is as follows:

$$\text{rate} = k[\mathrm{A}]$$

First-order Reactions

In a linear equation such as this, k is the proportionality constant. Without even knowing the value of k, you know that the rate is proportional to the concentration of A. Therefore, if the concentration is doubled, the rate will double. If the concentration is tripled, the rate will triple. Because the rate of the reaction is directly proportional to the first power of the concentration, reactions that fit this linear relationship are called *first-order reactions.*

In many decomposition reactions, the rate is directly proportional to the concentration of the single reactant. For reactions with more than one reactant, rate vs. concentration experiments can be carried out on each reactant individually. For example, consider this general reaction:

$$\mathrm{A(aq)} + \mathrm{2B(aq)} \rightarrow \mathrm{3C(aq)} + \mathrm{4D(aq)}$$

Experiments would be performed with an excess of reactant B, so its effect on the rate would be negligible; also, concentrations of A would be varied. Then further experiments would be performed with an excess of A, and the concentration of B would be varied. A rate vs. concentration relationship would be determined for each reactant. If each set of experiments with each reactant resulted in a linear relationship, you would say that the reaction is first order with respect to reactant A and first order with respect to reactant B.

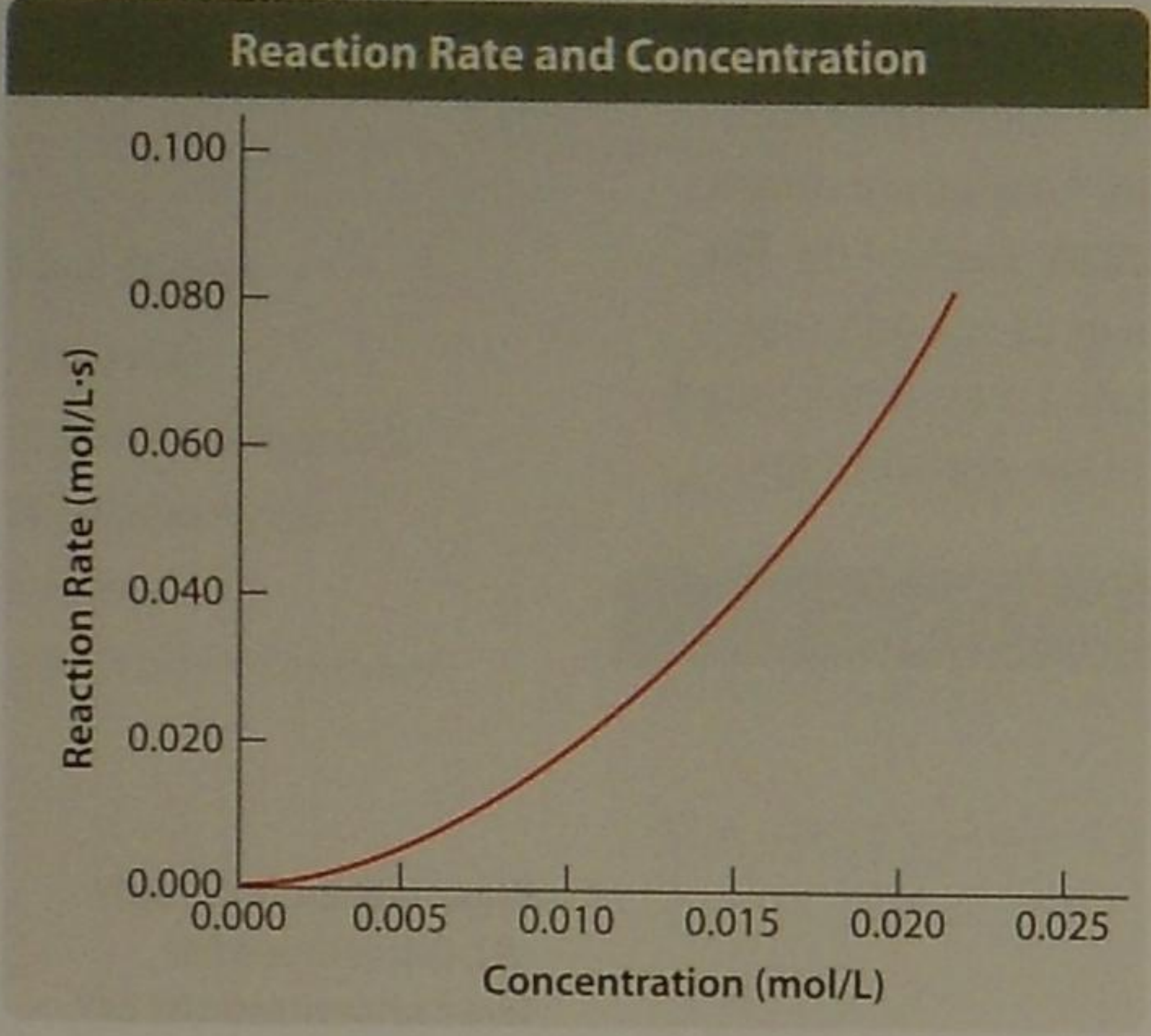


Figure 6.23 This graph represents reactions for which the rate is proportional to the square of a reactant. In the case of the reaction between chlorine dioxide and the hydroxide ion, the reaction is second order with respect to chlorine dioxide, but first order with respect to the hydroxide ion.

Second-order Reactions

However, many reactions are not first-order reactions with respect to a certain reactant. For example, in the reaction between chlorine dioxide and a hydroxide ion, a mixture of chlorate and chlorite ions are produced, as shown below.

$$2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(\ell)$$

Data from experiments on various concentrations of chlorine dioxide in an excess of hydroxide ions generate a graph like the one shown in **Figure 6.23**. The shape of this curve is parabolic. That is, it is half of a parabola, with its vertex at the origin of the co-ordinate system. The basic mathematical equation for a parabola with its vertex at the origin is $y = kx^2$. In this rate vs. concentration graph, y is the reaction rate, and x is the starting concentration of the reactant. Therefore, the equation can be written as follows:

$$\text{rate} = k[A]^2$$

The rate of the reaction is proportional to the square of the concentration of the reactant. A reaction that generates data that fit this parabolic curve is called a *second-order reaction*. If the concentration of the reactant is doubled, the rate of the reaction will increase by a factor of 2^2—it will be four times as fast. If the concentration is tripled, the rate will be 3^2, or nine times as fast.

Activity 6.3 Graphical Analysis of Reaction Rates vs. Concentration

In this activity, you will graph data for two different chemical reactions and then analyse the graphs to obtain a mathematical relationship between the reaction rate and the starting concentration of the reactant.

Consider the following two experiments.

Experiment 1 investigated this chemical reaction:

$$C_2H_5Br(g) + \text{heat} \rightarrow C_2H_4(g) + HBr(g)$$

Five trials were done for five different concentrations of bromoethane; the initial rates were determined from the graphs and the data in Table 1 were obtained.

Experiment 2 investigated this chemical reaction:

$$2NO_2(g) + \text{heat} \rightarrow 2NO(g) + O_2(g)$$

Five trials were done for five different concentrations of nitrogen dioxide. The rates were determined from the graphs and the data in Table 2 were obtained.

Table 1 Data Obtained from Experiment 1

$[C_2H_5Br]$ (mol/L)	Reaction Rate (mol/L·s)
1.00×10^{-3}	3.33×10^{-6}
2.00×10^{-3}	6.67×10^{-6}
3.00×10^{-3}	1.00×10^{-5}
4.00×10^{-3}	1.33×10^{-5}
5.00×10^{-3}	1.67×10^{-5}

Table 2 Data Obtained from Experiment 2

$[NO_2]$ (mol/L)	Reaction Rate (mol/L·s)
2.50×10^{-3}	4.69×10^{-8}
5.00×10^{-3}	1.88×10^{-7}
7.50×10^{-3}	4.22×10^{-7}
10.0×10^{-3}	7.50×10^{-7}
12.5×10^{-3}	1.17×10^{-6}

Procedure

For each set of data, draw a graph with reaction rate on the y-axis and starting concentration on the x-axis.

Questions

1. For each reaction, analyze the shape of the graph and determine the order of the reaction. Record your answer.
2. Write the general rate equation for each reaction, based on the orders of the reactions that were determined in question 1.
3. Calculate k for each experiment using representative data from each.
4. Write the rate equation for each reaction, based on your answers to questions 2 and 3.

The Rate Law

It is possible, although not common, for reactions to have an order of zero or a fraction such as $\frac{1}{2}$ or $\frac{3}{4}$. For example, a catalyzed reaction could be zero order with respect to one or all reactants if the catalyst was saturated. That is, a reaction rate would not change even with an increase in the amount of reactant, because there would be no more sites on the catalyst to which a reactant molecule could bind, if all sites were full (or saturated).

In general, the relationship between reaction rates and the concentration of reactants for the overall reaction can be written as follows:

$$\text{rate} = k[\text{A}]^m[\text{B}]^n$$

In this equation, m is the order of the reaction with respect to reactant A, and n is the order of the reaction with respect to reactant B. The proportionality constant, k, is called the *rate constant*. This equation is often called the *rate law*. Each reaction has its own rate law, with a specific value for the rate constant k, and for the order of the reaction, m and n, for each reactant, A and B. The order of the overall reaction is $m + n$. Note that some reactions have only one reactant whereas others have more than two reactants. Nevertheless, the form of the rate law is basically the same. Each constant—k, m, and n—must be calculated from experimental data. These constants can be determined graphically as discussed above or calculated mathematically. Mathematical methods for finding the rate law for specific reactions from experimental data are provided in Appendix B.

Learning Check

31. It would be tempting to use one graph of concentration versus time and measure the rate at different times and then use those data to plot a rate vs. concentration graph. Explain why this method could provide different results from the method you have learned.

32. What is the meaning of the term *initial rate*?

33. How is an initial rate measured? Explain the experimental procedure.

34. Explain how to obtain the data needed to make a plot of initial rate vs. starting concentration.

35. Describe the type of information that can be obtained from a plot of initial rate vs. starting concentration.

36. Given the general rate law, rate = $k[\text{A}]^m[\text{B}]^n$, explain the meaning of the constants, k, m, and n, and describe the methods for determining their value.

Reaction Mechanisms

The relationship between the concentration and the rate of a reaction can provide some general information about the **reaction mechanism**—a series of steps that occur during the process of converting reactants into products of a chemical reaction. In the discussion about activation energy, you read about an activated complex that was neither reactant nor product but a chemical species in between the two. In many reactions, there can be more than one activated complex, which means that the reaction takes place in more than one step. Each individual step in a multistep reaction is called an **elementary step**. The overall reaction, described by the balanced chemical equation, is a series of elementary steps that describe the progress of the overall reaction at the molecular level. How can the reaction order—the relationship between rate and concentration—reveal information about a reaction mechanism?

reaction mechanism a series of elementary steps that add to the overall reaction

elementary step a step in a series of simple reactions that represent the progress of the overall chemical reaction at the molecular level

Determining Reaction Mechanisms

A reaction between 2-bromo-2-methylpropane and sodium hydroxide, $NaOH(aq)$ occurs as follows:

$$(CH_3)_3CBr(aq) + Na^+(aq) + OH^-(aq) \rightarrow (CH_3)_3COH(aq) + Na^+(aq) + Br^-(aq)$$

Omitting the spectator ion, Na^+, the overall equation is:

$$(CH_3)_3CBr(aq) + OH^-(aq) \rightarrow (CH_3)_3COH(aq) + Br^-(aq)$$

Experiments that measure reaction rates using different concentrations of reactants show that this reaction is first order with respect to 2-bromo-2-methylpropane and zero order with respect to the hydroxide ion. The observation that changing the concentration of the hydroxide ion has no effect on the rate of the reaction is a strong indication that the reaction is not a simple, one-step reaction involving the hydroxide ion colliding with the other reactant. However, experiments cannot reveal the steps that take place on the molecular level.

Femtochemistry

In the 1980s, chemists began using laser pulses to monitor chemical reactions. These pulses are extremely short—in the order of magnitude of femtoseconds. One technique involves a series of pairs of pulses. The wavelength of the laser light and the time between pulses can be varied. In each pair of pulses, the first pulse supplies the activation energy to initiate a reaction. The absorbance of the second pulse can be measured to determine the absorbance characteristics of any activated complexes or intermediate chemical species created by the reaction. In this way, researchers can identify some chemical species that exist only momentarily. For example, activated complexes generally exist for only 10 to 1000 fs.

Data from laser pulses that occur every few femtoseconds show changes in the chemical bonds. This information allows chemists to determine reaction mechanisms as well as how the rate of a reaction is affected by different factors. The development of the femtosecond laser has led to a field of study called femtochemistry. A goal of femtochemistry is to determine reaction mechanisms in sufficient detail so that chemists are better able to develop techniques for controlling reaction rates and increasing the yield of desired products that can have industrial, environmental, and medical applications.

An example of a reaction that chemists have studied in detail is the decomposition of dinitrogen monoxide to form nitrogen and oxygen. The overall reaction is as follows:

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

However, nitrogen gas and oxygen gas are not formed directly. Instead, an oxygen atom, which is not represented in the balanced chemical equation, is briefly produced in the first elementary step of the overall reaction. (Note that states of matter are generally not shown in chemical equations showing elementary steps.)

$$N_2O \rightarrow N_2 + O$$

The oxygen atom can then react with another molecule of dinitrogen monoxide to produce nitrogen and oxygen. This reaction is the second elementary step of the overall reaction:

$$N_2O + O \rightarrow N_2 + O_2$$

The overall chemical reaction is the sum of the elementary steps:

$$\begin{array}{ll} \textit{Step 1:} & N_2O \rightarrow N_2 + O \\ \textit{Step 2:} & N_2O + O \rightarrow N_2 + O_2 \\ \hline \textit{Sum of reactions:} & 2N_2O + \cancel{O} \rightarrow 2N_2 + \cancel{O} + O_2 \\ \textit{Overall reaction:} & 2N_2O \rightarrow 2N_2 + O_2 \end{array}$$

intermediate a chemical species that appears in the elementary steps of a chemical reaction but not in the overall balanced chemical equation

The oxygen atom that is briefly produced in the first elementary step is called an **intermediate**, because it appears in the elementary steps but not in the balanced equation that represents the overall chemical reaction. An intermediate formed in an earlier elementary step is always consumed in a subsequent elementary step.

The Rate-determining Step

The rate of a reaction that has more than one elementary step is determined by the rate at which the slowest elementary step proceeds. Consider a line of vehicles on a road that is too narrow for one vehicle to safely pass another, as shown in **Figure 6.24**. The entire line of vehicles can proceed only as fast as the slowest vehicle is travelling. Similarly, the overall rate of a chemical reaction is dependent on the rate at which the slowest step occurs. The slowest elementary step is often called the *rate-limiting step* or the **rate-determining step**.

rate-determining step the slowest step among all the elementary steps in a specific multistep reaction, and which determines the rate of the overall chemical reaction

Figure 6.24 The overall rate of travel for these vehicles is limited by the speed of the car at the front of the line of traffic. In a similar way, the overall rate of a chemical reaction cannot be faster than its slowest elementary step.

An example of a three-step reaction, that of nitrogen monoxide with hydrogen gas to form nitrogen gas and water, is shown below:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

Of the three elementary steps that make up the overall chemical reaction, the first and third proceed relatively quickly, but the second elementary step proceeds slowly.

Step 1: $2NO \rightarrow N_2O_2$ (fast)
Step 2: $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)
Step 3: $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

Therefore, the second step is the rate-determining step. Each elementary step has its own activation energy, as shown in **Figure 6.25**. Because the activation energy for step 2 is higher than for steps 1 or 3, step 2 determines the rate at which the overall reaction proceeds.

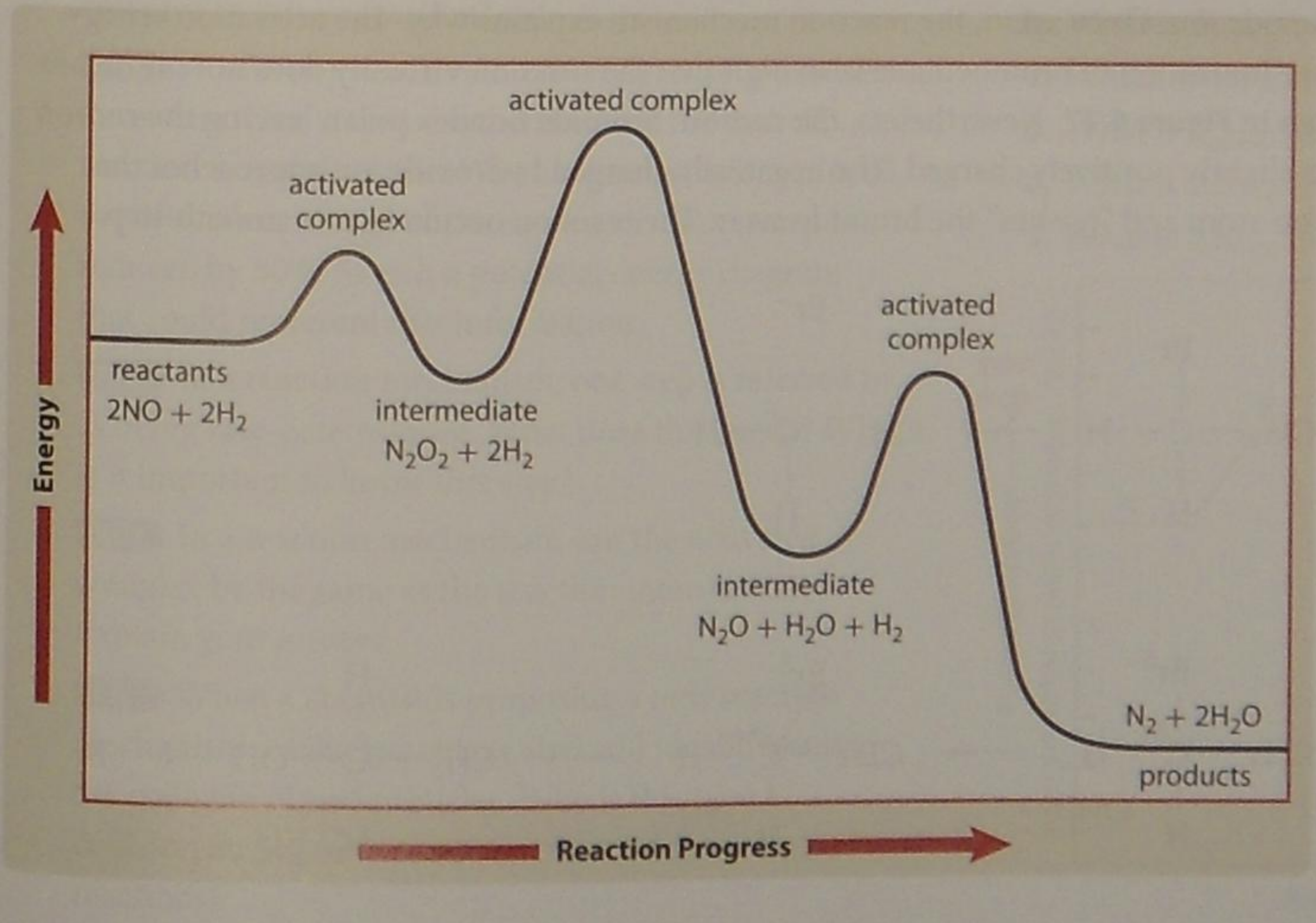


Figure 6.25 The three "hills" in this potential energy diagram represent the activation energies for the three elementary steps that make up the overall reaction. The second hill is highest, indicating that the second elementary step has the highest activation energy and is therefore the rate-determining step.

A Proposed Reaction Mechanism

A basic understanding of multistep reactions and rate-determining steps makes it possible to analyze the earlier reaction between 2-bromo-2-methylpropane and the hydroxide ion to find out how a reaction can be zero order with respect to one reactant.

The mechanism of the reaction is shown in **Figure 6.26**. The first step involves only the 2-bromo-2-methylpropane, which ionizes. This step is very slow relative to the second step. The second step, during which the hydroxide ion forms a covalent bond with the positively charged ion from the first step, is extremely fast. This reaction is so fast that increasing the concentration of the hydroxide ion has no effect on the overall speed of the reaction, because, in a sense, the hydroxide ions that are present are "waiting" for positively charged ions to form. The addition of more hydroxide ions will not speed up the formation of the positively charged ion from the first step. The instant that this positively charged ion forms, it reacts with either a bromide ion or a hydroxide ion. When the final product 2-methylpropan-2-ol is formed, it is quite stable, because the activation energy for the reverse reaction is so large that the reaction is essentially irreversible.

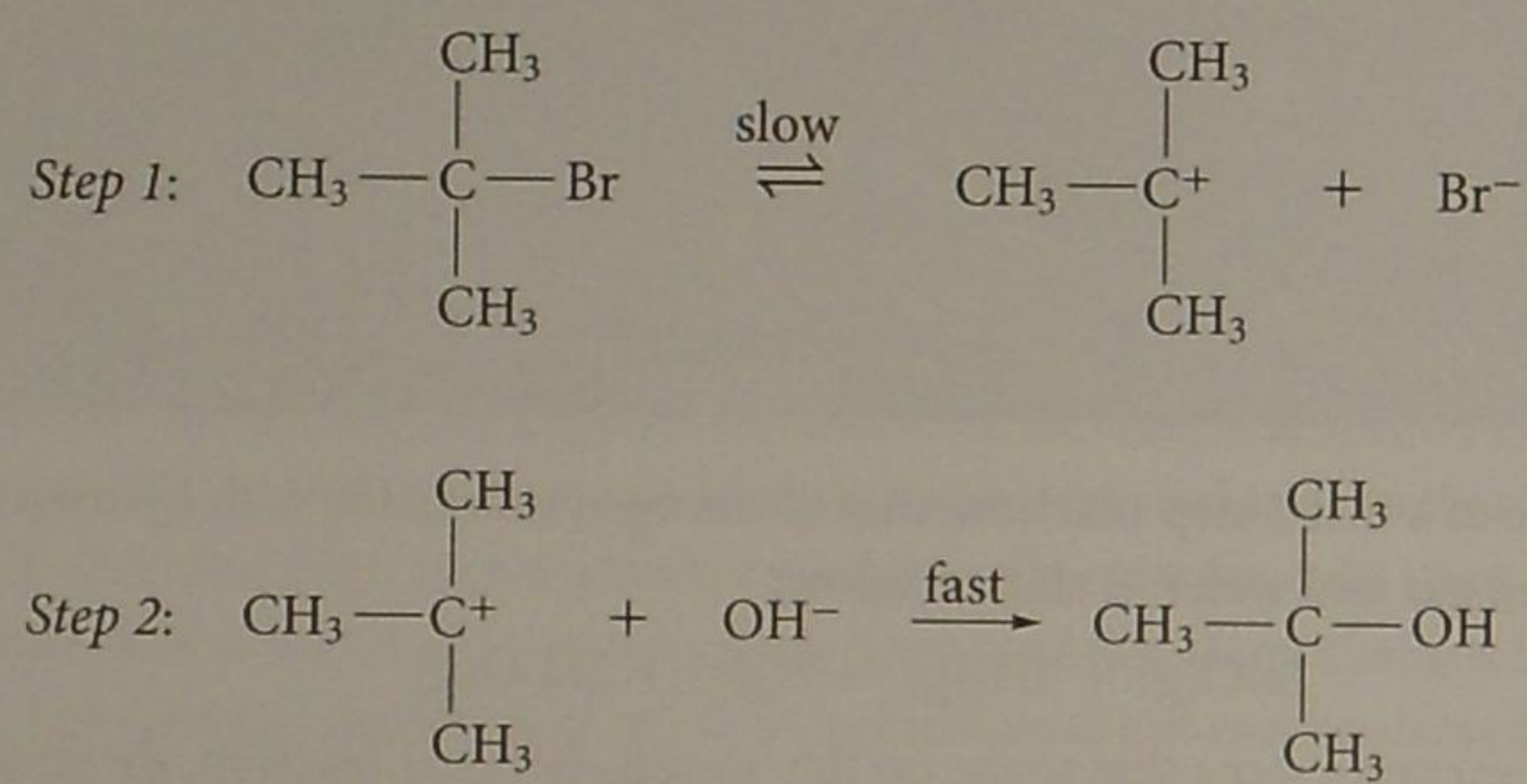


Figure 6.26 The rate-determining step is the first step, which involves only the 2-bromo-2-methylpropane. Thus, doubling the concentration doubles the speed of step 1, making it a first-order reaction. Step 2 is so fast that it is dependent on the completion of step 1 and independent of the concentration of hydroxide ions. Therefore, the reaction is zero order with respect to hydroxide ions.

In comparison, the reaction between bromoethane, $CH_3CH_2Br(aq)$, and the hydroxide ion might be expected to follow the same process.

$$CH_3CH_2Br(aq) + OH^-(aq) \rightarrow CH_3CH_2OH(aq) + Br^-(aq)$$

However, this reaction is first order with respect to both the bromoethane and the hydroxide ion. Once again, the reaction mechanism explains why. The activation energy for the ionization of bromoethane is so high that the reaction virtually does not occur, as shown in **Figure 6.27**. Nevertheless, the carbon–bromide bond is polar, leaving the carbon atom slightly positively charged. The negatively charged hydroxide ion approaches the carbon atom and "pushes" the bromide away. The reaction occurs in one smooth step.

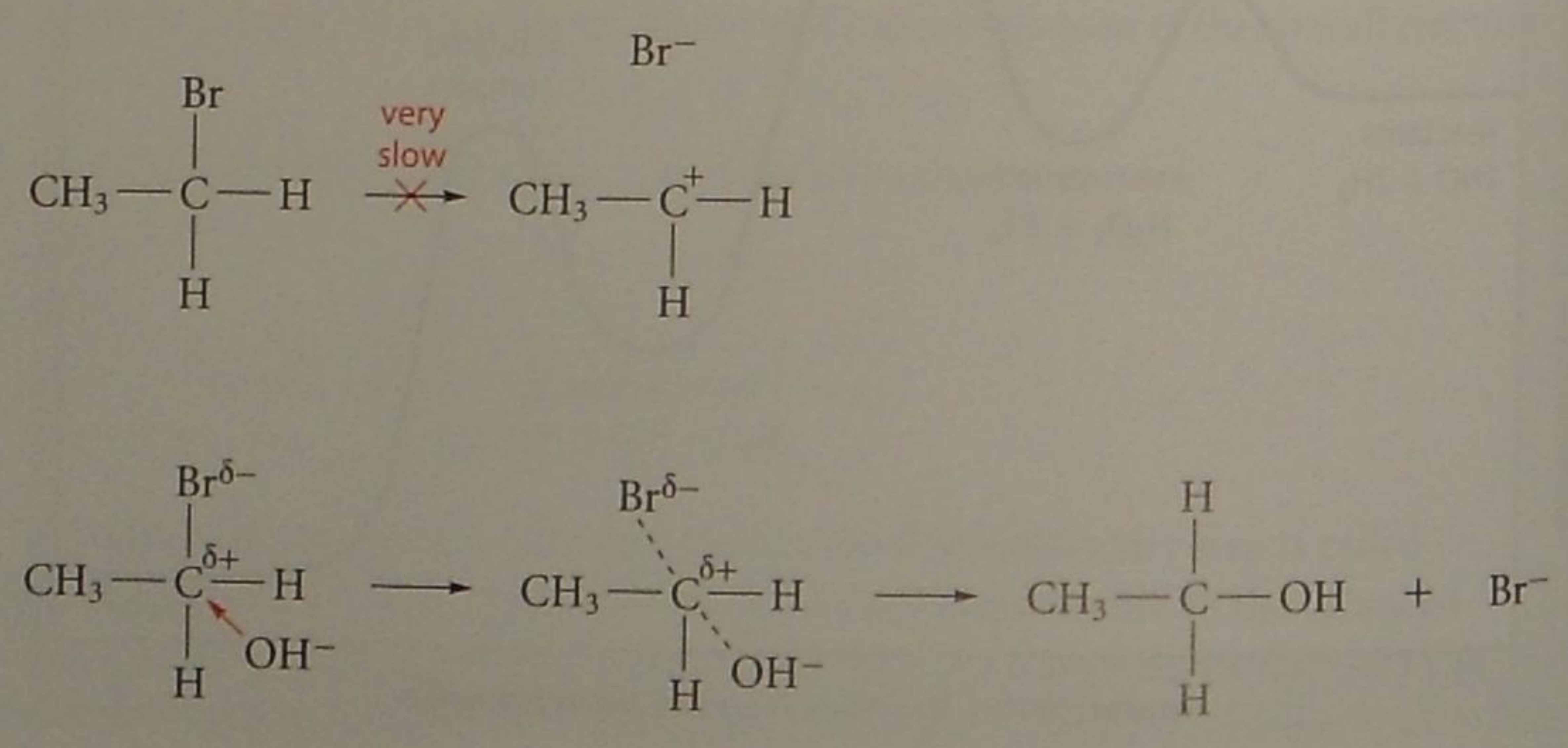


Figure 6.27 Doubling the concentration of bromoethane would double the rate of the reaction, and doubling the concentration of the hydroxide ion would also double the rate. Therefore, doubling the concentration of both reactants would quadruple ($2 \times 2 = 4$) the reaction rate.

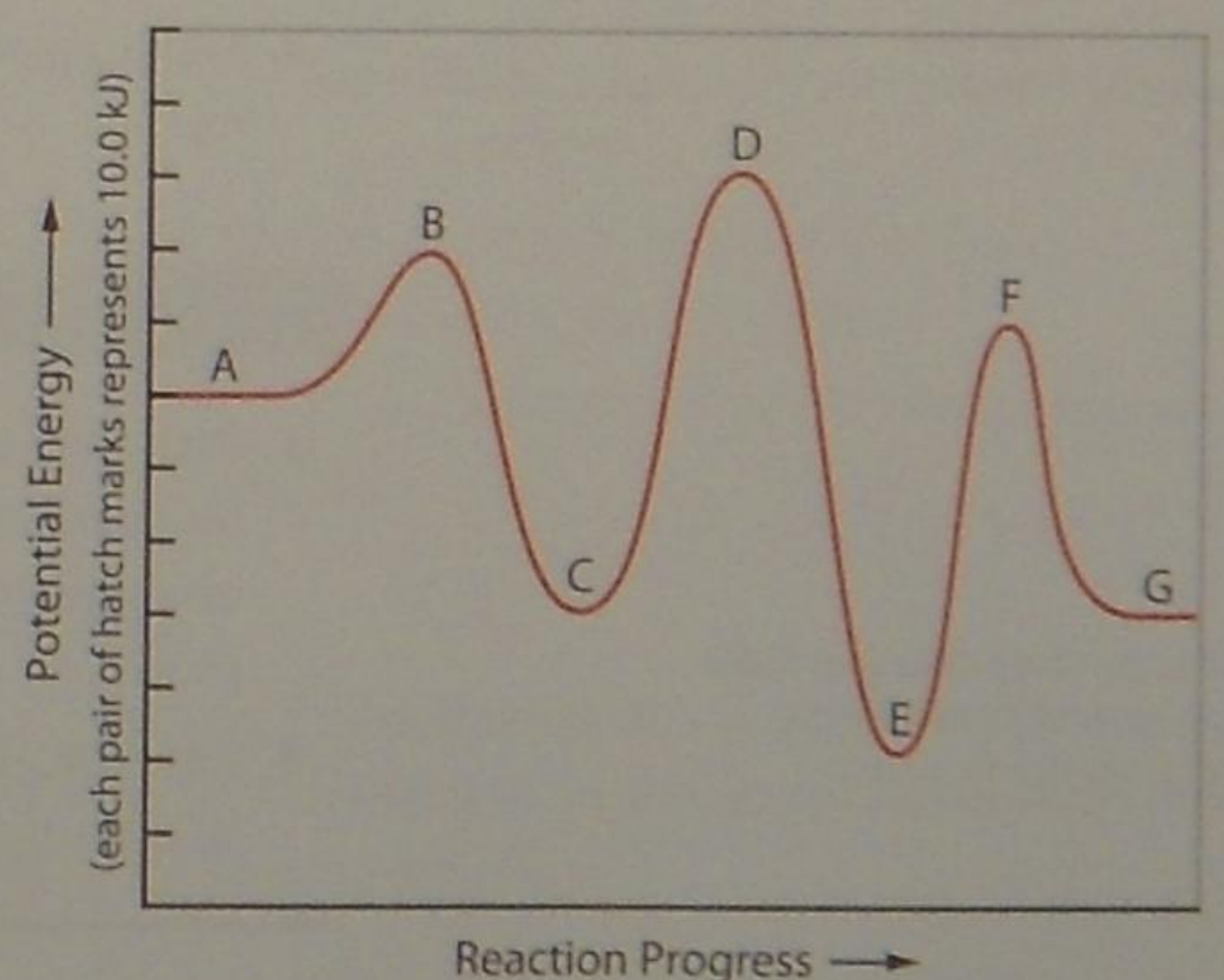
Section 6.3 Review

Section Summary

- To determine the relationship between the rate of a reaction and the concentration of reactants, several experiments must be carried out and the initial rates of each reaction determined.
- The rate of a reaction can be directly proportional to the concentration of a reactant, or proportional to the square of the concentration of a reactant.
- The rate law for a chemical reaction is a mathematical relationship that must be experimentally determined.
- Elementary steps are a series of simple reactions that describe the progress of an overall reaction at the molecular level.
- The slowest elementary step in a chemical reaction determines the rate of the overall reaction.
- Femtochemistry allows chemists to observe the properties of activated complexes and intermediates in chemical reactions and thus to determine reaction mechanisms.

Review Questions

1. K/U Which of the factors that affect the rate of a reaction is put into quantitative terms in the rate law expression?
2. K/U What does a balanced chemical equation indicate about the rate law for a reaction?
3. C Refer to **Figure 6.25**. Write your own caption for this diagram. The caption should also include an explanation that clearly distinguishes between the terms *activated complex* and *intermediate*.
4. K/U Explain what an initial rate is.
5. C You must plan an investigation to determine how to double the rate of a reaction. You have been told that the rate law for the reaction below is rate $= k[A]^2$.
   $$2A(aq) + B(s) \rightarrow \text{product}$$
   Your partner suggests that the rate law does not need to be used. Doubling the surface area of reactant B would double the reaction rate. What response would you give to this suggestion?
6. T/I A two-step reaction mechanism is proposed for a reaction. One step is exothermic, but the overall reaction is endothermic. When a catalyst is introduced, the activation energy of the rate-determining step is reduced by 50%. Sketch a potential energy diagram that could represent this information.
7. K/U In a reaction mechanism, one step is referred to as being rate-determining. What does this mean? Why is it important to know this step?
8. K/U In a reaction mechanism, can the activated complex be the same as the reaction intermediate? Explain your answer.
9. A When a chemist is proposing a new reaction mechanism, each elementary step will ideally involve the collision of two particles. Why is this type of collision an important characteristic of elementary reactions?
10. T/I The reaction mechanism below has been proposed by a chemist working to convert chloroform to carbon tetrachloride.
    Step 1: $Cl_2 \rightarrow 2Cl$
    Step 2: $Cl + CHCl_3 \rightarrow HCl + CCl_3$
    Step 3: $Cl + CCl_3 \rightarrow CCl_4$
    a. Write the overall equation for this reaction mechanism.
    b. Is there a catalyst in this reaction? Give a reason for your answer.
    c. Identify any intermediates in this mechanism. Give a reason for your answer.
    d. The rate law for the overall reaction is rate $= k[CHCl_3]$. Which step would likely be the rate-determining step? Give a reason for your answer.
11. T/I Examine the potential energy diagram below and answer the following questions.
    a. Which letter(s) represents an activated complex?
    b. What is $E_{a(rev)}$ for step 2?
    c. Which letter(s) represents a reaction intermediate?
    d. What is $E_{a(fwd)}$ for step 3?
    e. What is ΔH_{fwd} for the endothermic step?
    f. What is ΔH_{fwd} for the overall reaction?



Plan Your Own
INVESTIGATION

6-A

Skill Check

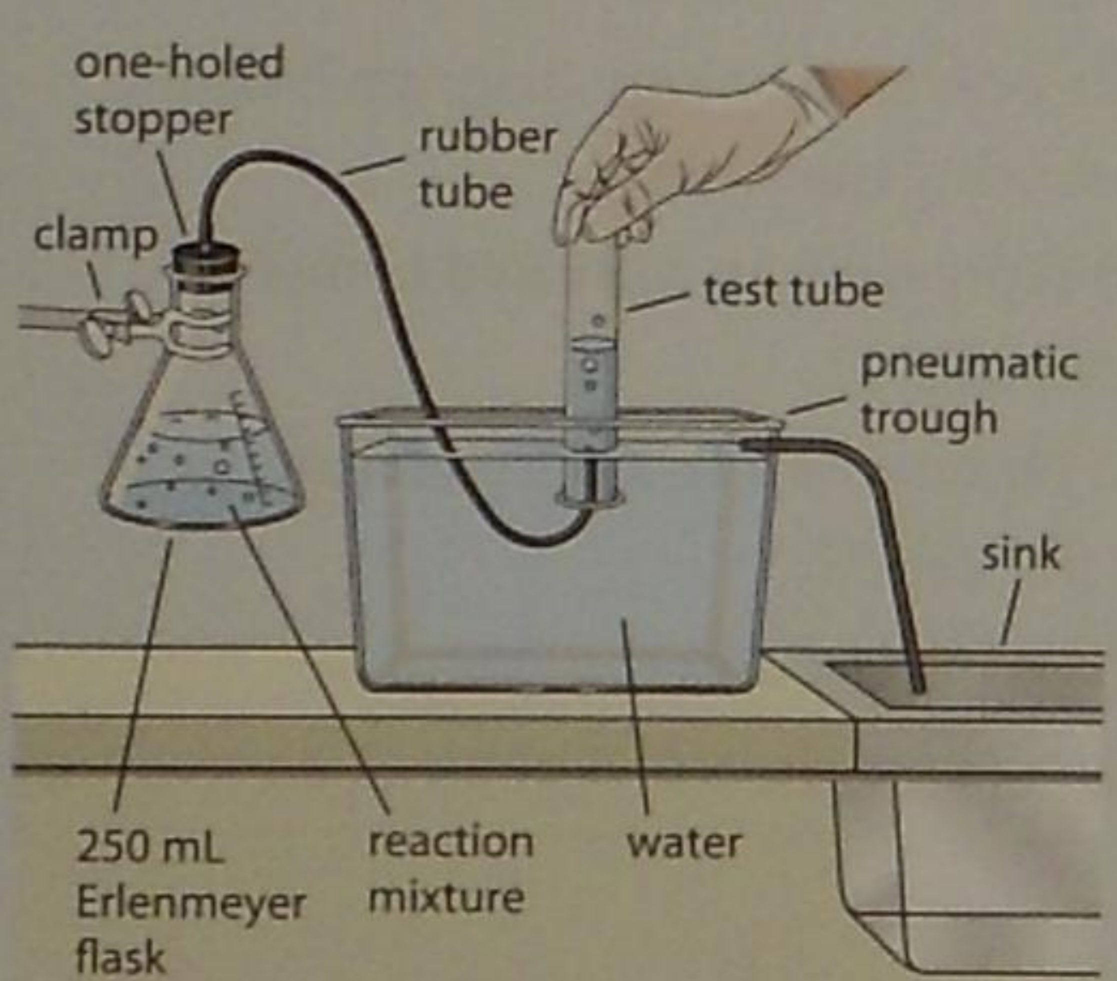
- ✓ Initiating and Planning
- ✓ Performing and Recording
- ✓ Analyzing and Interpreting
- ✓ Communicating

Safety Precautions

- Wear safety eyewear throughout this investigation.
- Wear a lab coat or apron throughout this investigation.
- Beware of electrical shock hazard if an electric kettle or hot plate is used.

Suggested Materials

- vinegar (5.0% (m/v), or 0.83 mol/L)
- $NaHCO_3(s)$ or $CaCO_3(s)$
- 500 mL of 0.83 mol/L $HCl(aq)$
- additional materials and equipment appropriate to your experimental method



Go to **Organizing Data in a Table** in **Appendix A** for information about designing data tables.

Examining Reaction Rates

You will design an investigation to determine factors affecting the rate of this reaction:

$$CH_3COOH(aq) + NaHCO_3(aq) \rightarrow NaCH_3COO(aq) + CO_2(g) + H_2O(g)$$

These factors may include, but are not limited to, concentration of reactants, temperature of reactants, nature of reactants, and surface area.

Pre-Lab Questions

1. Aside from collecting carbon dioxide by downward displacement of water, as shown in the diagram, how else could you monitor the rate of CO_2 production in this investigation?
2. If you use the method illustrated in the diagram, why must the water be saturated with CO_2?

Question

What factors affect the rate of a chemical reaction?

Plan and Conduct

1. Decide on a method to measure the amount of CO_2 "lost" per unit of time. Write up a complete, detailed procedure and, with your teacher's permission, collect and set up the apparatus you will need.
2. Prepare a table to record observations. Remember to manipulate only one variable at a time. Collaborate with other groups who are measuring the CO_2 in the same manner and pool your results. Also, exchange results with other groups that are testing different factors.
3. Carry out as many trials as time permits.
4. Clean up your work area as instructed by your teacher.

Analyze and Interpret

1. Explain quantitatively how the factors that you investigated affected the reaction rate.

Conclude and Communicate

2. Make a general statement about the effect of each factor on the reaction rate.

Extend Further

3. **INQUIRY** One of the products of the reaction is a gas. Would changing the pressure of the system affect the rate of the reaction? Design an investigation that would measure the rate of the reaction under various pressures.
4. **RESEARCH** Find out about industrial processes carried out under pressure. What is the effect of pressure, and why is the method used?

Plan Your Own INVESTIGATION

6-B

The Effect of a Catalyst on the Decomposition of $H_2O_2(aq)$

Skill Check

- ✓ Initiating and Planning
- ✓ Performing and Recording
- ✓ Analyzing and Interpreting
- ✓ Communicating

Safety Precautions

- The reaction mixture will get hot. Handle all glassware with care.
- 6% hydrogen peroxide, $H_2O_2(aq)$, is an irritant. Wear safety eyewear, gloves, and a laboratory apron.

Materials

- 40 mL of 6% (m/v) $H_2O_2(aq)$
- 20 mL of 1.0 mol/L NaI(aq)
- masking tape or grease pencil
- 100 mL beakers
- 10 mL graduated cylinders
- 250 mL Erlenmeyer flask
- clock with a second hand or stopwatch
- water
- one-holed stopper, fitted with a piece of glass tubing (must be airtight)
- rubber tubing to fit glass tubing (must be airtight)
- large test tube
- pneumatic trough or large beaker
- electronic balance accurate to 0.001 g

Go to **Constructing Graphs** in **Appendix A** for help with drawing graphs.

You will investigate the effect of the $I^-(aq)$ ion as a catalyst on the decomposition of hydrogen peroxide, $H_2O_2(aq)$. The gas produced can be measured as a decrease in mass of the system or by the downward displacement of water.

Pre-Lab Questions

1. Write the chemical equation for the decomposition reaction in this investigation.
2. How can you deal with the reaction vessel heating up during the reaction?
3. What factors could affect the rate of this reaction?

Prediction

Predict the effects of changing the concentration of a catalyst and the concentration of hydrogen peroxide on the rate of decomposition of hydrogen peroxide.

Plan and Conduct

1. Write a detailed procedure to test your prediction. Consider which variables will be constant and which will be changed. Include a data table.
2. Check your plan to ensure that all safety requirements are addressed.
3. Your teacher must approve your procedure before you can begin the experimental work.
4. Clean up your work area when you are finished.

Analyze and Interpret

1. Was there any evidence of a gas being produced before the catalyst was added? Explain.
2. Plot a graph of rate of formation of gas (in mL or g) vs. $[I^-]$ for the trials you conducted.
3. What does the graph in question 2 indicate about the effect of the iodide ion on the reaction rate?
4. Plot a graph of the formation of gas (in mL or g) vs. $[H_2O_2]$ for the trials you conducted.
5. What does the graph in question 4 indicate about the effect of the concentration of hydrogen peroxide on the reaction rate?
6. Evaluate the method you used. What changes or additions would you make if you could repeat the investigation?

Conclude and Communicate

7. Explain the effects of changing the concentration of iodide catalyst and changing the concentration of the reactant, hydrogen peroxide, on the rate of the decomposition of hydrogen peroxide.

Thought Lab
INVESTIGATION

6-C

Skill Check

Initiating and Planning
- ✓ Performing and Recording
- ✓ Analyzing and Interpreting
- ✓ Communicating

Exploring Catalysts in Industry

Catalysts are widely used in many industries. The petroleum industry uses catalysts for many processes, including the refining of oil for fuels and for the synthesis of polymers to make plastics and fibres. Other areas of industry that depend on catalysts include the food industry, pollution control, environmental protection, health, and new sources of energy.

Biological catalysts—enzymes—are also used in industry. The discovery of one particular enzyme with the right characteristics opened up the world of DNA research and such applications as DNA fingerprinting.

Question

What are the social and industrial benefits of a specific catalyst and what characteristics make this catalyst useful?

Organize the Data

1. Work in groups of 3 or 4. Each student should research a variety of catalysts used in industry.
2. Narrow your research to focus on one specific catalyst or catalyzed process. Suggest this catalyst to your group as a topic for your presentation.
3. As a group, review the suggested topics from each member and agree on one to study in more detail. Assign each member a task to complete.

Analyze and Interpret

1. Your research and report should include as many of the following topics as can be applied to your chosen catalyst or catalyzed process.
   - What is the chemical nature of your catalyst? For example, is it an inorganic compound containing a transition metal, is it an enzyme, or is it some other compound?
   - Is your catalyst a heterogeneous catalyst or a homogenous catalyst? (If you have not encountered these terms, find out what they mean.)
   - What is the mechanism of action of your catalyst? That is, how does it speed the reaction(s) involved in the overall process of manufacturing the product?
   - What product(s) is your catalyst used to manufacture?
   - How is your catalyst beneficial to the industry that uses it?
   - How is your catalyst beneficial to society or the environment?
2. What was the most interesting fact that you learned while researching and compiling your topic?

Conclude and Communicate

3. Organize the information that your group compiled into a multimedia presentation, a Web page, or a news item. Make your presentation available to your class for discussion and assessment.

Chapter 6 SUMMARY

Section 6.1 Rates of Reaction

Reaction rates are determined by the activation energy, but not by the amount of energy gained or lost during the reaction.

Key Terms
average rate of reaction
instantaneous rate of reaction
reaction rate

Key Concepts

- A reaction rate is the speed at which a chemical reaction occurs. A reaction rate is measured by the change in the amount of reactants consumed or products formed over a given time interval.
- A reaction rate is always expressed as a positive value.
- The instantaneous rate of a reaction is the rate of the reaction at a particular point in time.
- The average rate of a chemical reaction is the change in the concentration of a reactant or product per unit time over a given time interval.
- Any measurable property that is related to a change in the amount of a reactant or product during a chemical reaction can be used to determine the reaction rate.

Section 6.2 Collision Theory and Factors Affecting Rates of Reaction

For a reaction to occur, reactants must collide in the correct orientation and with enough kinetic energy to overcome the activation energy barrier. The rate of a reaction is affected by factors that include the nature of the reactants, temperature, concentration, surface area of solid particles, and the presence of a catalyst.

Key Terms
activated complex
activation energy, E_a
catalyst
collision theory
enzyme

Key Concepts

- According to collision theory, a reaction will occur only if the reactants collide with the correct orientation and energy equal to or greater than the activation energy, E_a.
- When reactants collide with sufficient energy to overcome the activation energy barrier, they form an activated complex, which is an unstable transition state.
- A potential energy diagram can represent reversible reactions. For the reverse reaction, follow the curve from right to left.
- Factors that affect the rate of a chemical reaction include the nature of the reactants, the concentration of a solution, temperature, the pressure of gaseous reactants, the surface area of solid particles of the reactants, and the presence of a catalyst.
- A catalyst is a substance that increases the rate of a reaction but is itself unchanged at the end of the reaction.
- Biological catalysts are called enzymes and are specialized to catalyze only one or a few specific reactions. Enzymes can be used in industrial applications to reduce the use of chemicals that can adversely affect the environment.

Section 6.3 Reaction Rates and Reaction Mechanisms

The relationship between the rate of a reaction and the concentration of the reactants for any given reaction is indicated by the exponent of the concentration of the reactions in the expression rate = $k[A]^m$. Many overall reactions are the sum of several elementary steps.

Key Terms
elementary step
initial rate
intermediate
rate-determining step
reaction mechanism

Key Concepts

- To determine the relationship between the rate of a reaction and the concentration of reactants, several experiments must be carried out and the initial rates of each reaction determined.
- The rate of a reaction can be directly proportional to the concentration of a reactant, or proportional to the square of the concentration of a reactant.
- The rate law for a chemical reaction is a mathematical relationship that must be experimentally determined.
- Elementary steps are a series of simple reactions that describe the progress of an overall reaction at the molecular level.
- The slowest elementary step in a chemical reaction determines the rate of the overall reaction.
- Femtochemistry allows chemists to observe the properties of activated complexes and intermediates in chemical reactions and thus to determine reaction mechanisms.

Chapter 6 REVIEW

Knowledge and Understanding

Select the letter of the best answer below.

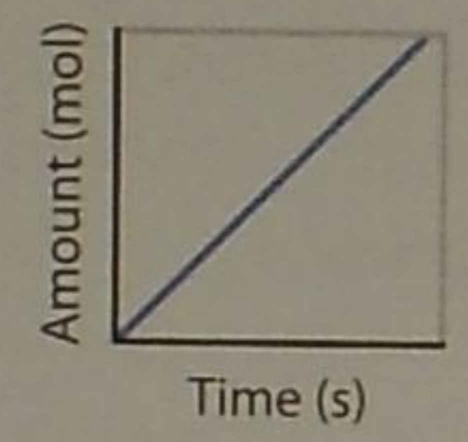
1. Which expression could be a unit for the measurement of rate of reaction?
   a. $\frac{mol^2}{L^2}$
   b. $\frac{L \cdot min}{mol}$
   c. $\frac{mol}{L}$
   d. $\frac{mol}{L \cdot s}$
   e. s^{-1}

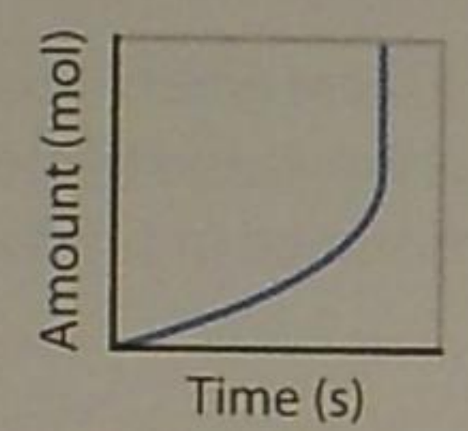
2. Which one of the following features of a chemical reaction is the best indicator as to whether the reaction will proceed quickly at room temperature?
   a. reaction mechanism
   b. activation energy
   c. balanced equation
   d. rate law equation
   e. ΔH

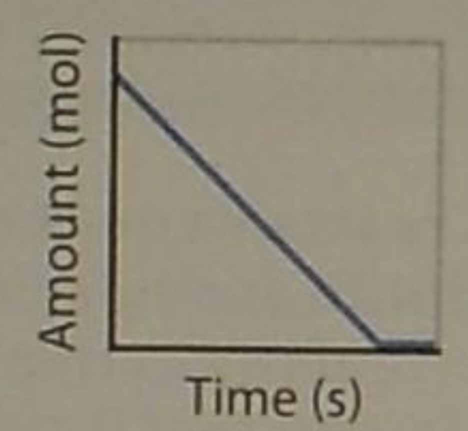
3. For the reaction represented as $A + B \rightarrow C$, which statement is correct concerning the formation of product C?
   a. C forms half as fast as the reactants A and B are used up.
   b. C forms twice as fast as the reactants A and B are used up.
   c. C forms at the same rate as each of A and B are used up.
   d. C forms at a rate independent of the rate of change in reactants A and B.
   e. C forms at a rate equal to the sum of the rate at which reactants A and B are used up.

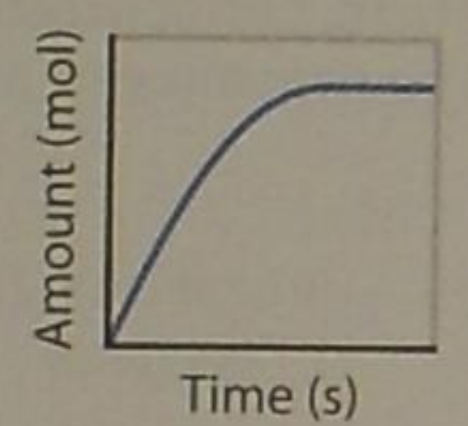
4. Which property cannot be used to measure the rate of the reaction given by the equation below?
   $$CaC_2(s) + H_2O(\ell) \rightarrow Ca(OH)_2(aq) + C_2H_2(g)$$
   a. change in concentration of reactants
   b. change in pH
   c. change in mass of $CaC_2(s)$
   d. change in volume of $C_2H_2(g)$
   e. change in concentration of $Ca^{2+}(aq)$

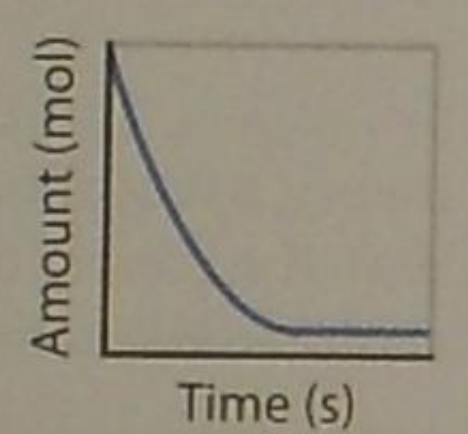
5. A decrease in temperature will decrease the rate of a reaction principally because
   a. the particles have less potential energy at the lower temperature.
   b. the particles in the reactants move closer together at a lower temperature.
   c. the activation energy for the reaction increases with a decrease in temperature.
   d. the activation energy for the reaction decreases with a decrease in temperature.
   e. fewer particles have energy equal to or greater than the activation energy.

6. Which graph correctly shows the change in amount of product as the reaction shown below proceeds to completion?
   $$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$$
   a.


   b.


   c.


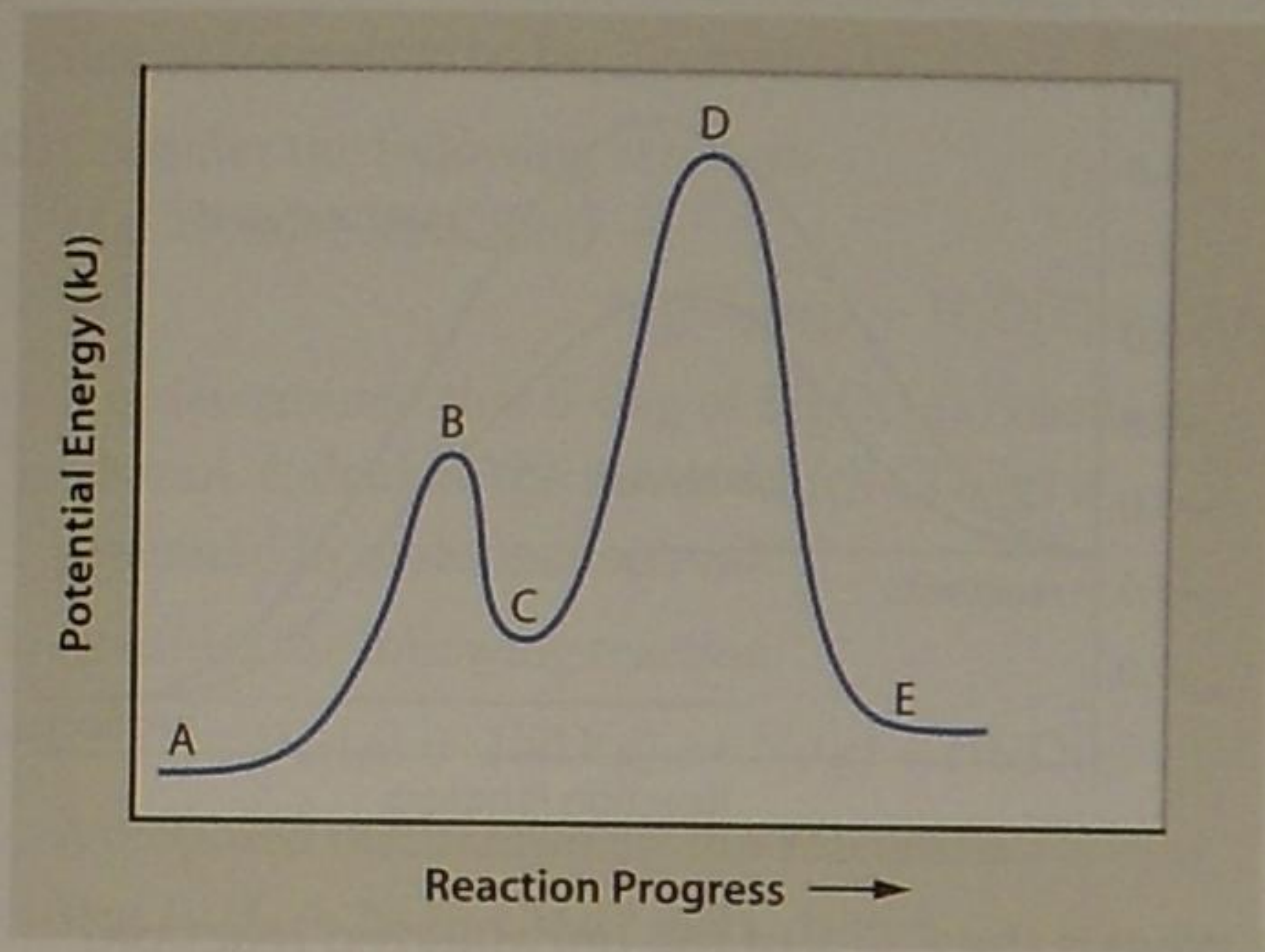
   d.


   e.


7. A reaction is exothermic in the forward direction. Which statement is correct with regard to the activation energy of the reverse reaction?
   a. $E_{a(rev)} = E_{a(fwd)} + \Delta H_r$
   b. $E_{a(rev)} = 2E_{a(fwd)} + \Delta H_r$
   c. $E_{a(rev)} = E_{a(fwd)} - 2\Delta H_r$
   d. $E_{a(rev)} = E_{a(fwd)} - \Delta H_r$
   e. $E_{a(rev)} = 2E_{a(fwd)} - \Delta H_r$

8. The expression for the rate law may be written in the general form:
   $$\text{rate} = k[A]^m[B]^n$$
   Experimental evidence indicates that for a particular reaction, $m = 2$ and $n = \frac{1}{2}$. What is the overall order of the reaction?
   a. 1
   b. $2\frac{1}{2}$
   c. 4
   d. $1\frac{1}{2}$
   e. $\frac{3}{2}$

9. Examine the potential energy diagram shown below. Identify the letter that represents the position(s) of a reaction intermediate.



a. E
b. B and D
c. B, C, and D
d. C
e. A

10. Which of the following statements about an activated complex is accurate?
a. It always breaks down to form product molecules.
b. It occurs only in endothermic processes.
c. It has lower chemical potential energy than reactants or products.
d. It is a stable substance.
e. It occurs at the transition state of the reaction.

11. Which of the following most closely applies to collision theory?
a. kinetic molecular theory
b. the first law of thermodynamics
c. Boyle's law
d. atomic theory
e. the law of definite proportions

12. For the single displacement reaction,

$$Zn(s) + CuSO_4(aq) \rightarrow Cu(s) + ZnSO_4(aq)$$

select the factor from the list below that would have the greatest effect on the rate of reaction.
a. increase the amount of Zn(s)
b. increase the amount of Cu(s)
c. stir the reaction
d. increase the concentration of $CuSO_4(aq)$
e. increase the pressure on the system

13. A catalyst will increase the rate of a reaction by
a. decreasing ΔH for both the forward and reverse reactions.
b. increasing the number of collisions between particles.
c. providing an alternate reaction mechanism having a lower activation energy.
d. eliminating the rate-determining step in the reaction mechanism.
e. acting as an intermediate in the reaction mechanism.

14. Two test tubes, A and B, contain samples of zinc that are equal in mass and have the same surface area. Equal concentrations and amounts of sulfuric acid are added to the test tubes. A catalyst is added to test tube A. Why must the zinc samples have identical surface areas?
a. Test tube B is the control.
b. Surface area is another factor that could affect the rate of the reactions.
c. Test tube A is the control.
d. Both (a) and (b) are correct.
e. Both (b) and (c) are correct.

Answer the questions below.

15. State a quantitative definition of rate of reaction.

16. What would be a possible unit for measuring the rate of reaction for each of the following?
a. $O_2(g)$ is produced in a reaction.
b. Gases are produced in a closed container.
c. Acid is used up during a reaction.

17. How does the total pressure on a system affect the rate of reaction between
a. two reactants in the gas state?
b. two reactants in an aqueous solution?

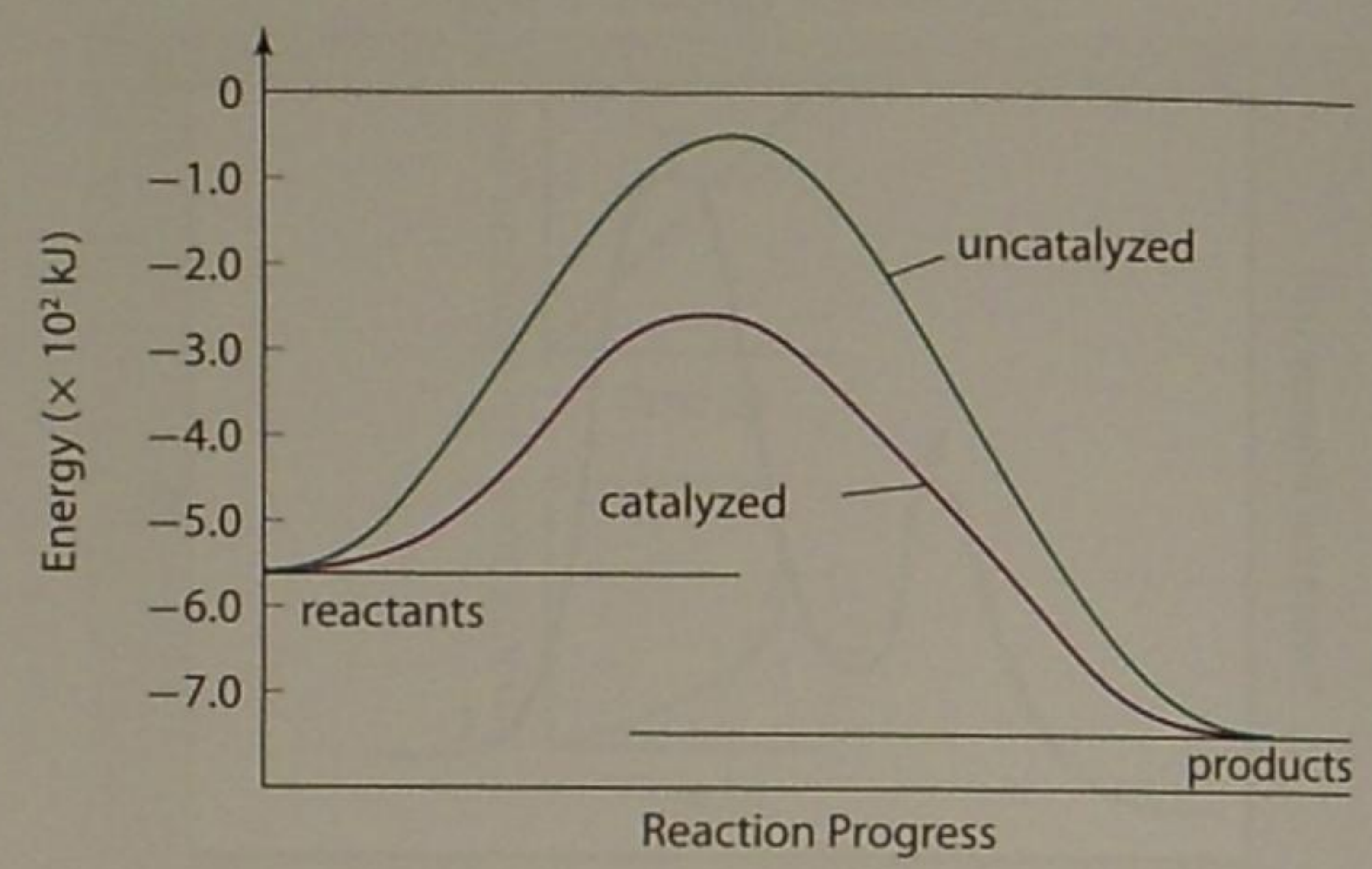
18. Suggest two reasons why some reactions are difficult to start.

19. There are several important concepts related to the rates of reactions.
a. At what point in a chemical reaction does the initial reaction rate occur?
b. How can the initial rate of a chemical reaction be determined?
c. Is it possible, during a reaction, for the instantaneous and average rates of reaction to have the same value? How would you know if this is the case?

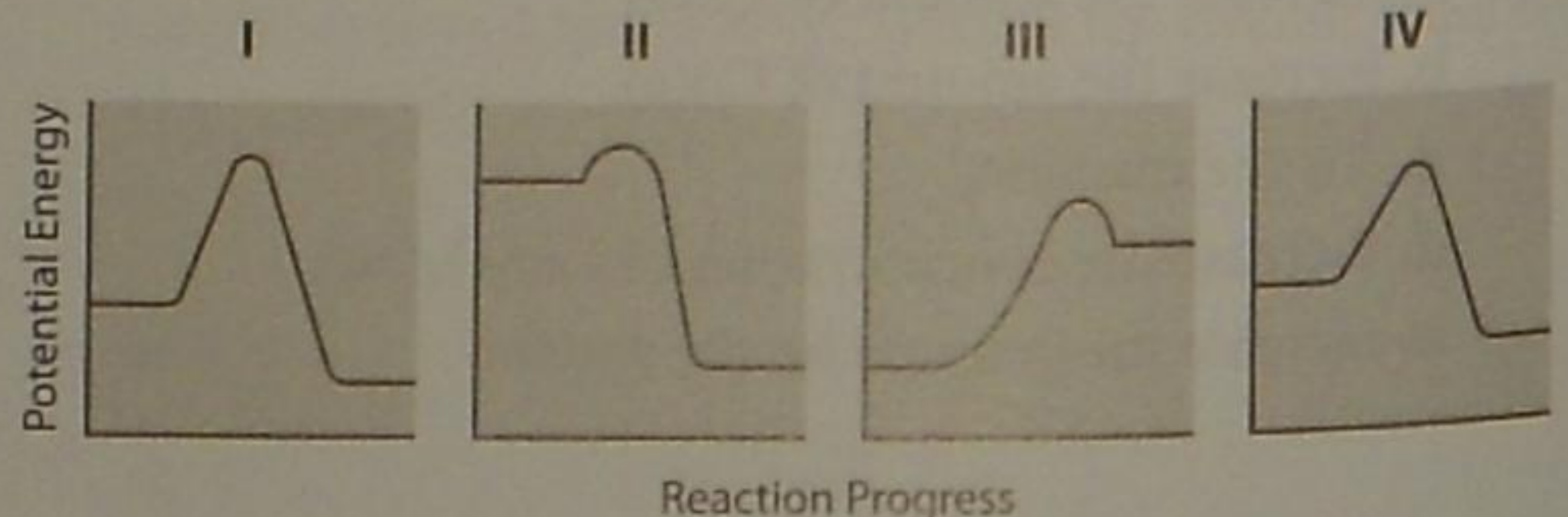
20. Catalysts can significantly alter the rates of many chemical reactions.
   a. How does a catalyst speed up the rate of a reaction?
   b. The net ionic equation for the reaction between lead(II) ions, $Pb^{2+}(aq)$, and carbonate ions, $CO_3^{2-}(aq)$, is shown below as it occurs in aqueous solution. Would a catalyst affect the rate of this reaction? Give a reason for your answer.
   $Pb^{2+}(aq) + CO_3^{2-}(aq) \rightarrow PbCO_3(s)$
21. A reaction is carried out between two gases in a closed system of fixed volume. Why does an increase in the partial pressure of a gaseous reactant increase the rate of reaction?
22. In terms of collision theory, how does stirring affect the rate at which a solid dissolves in water?
23. What is the difference between the activation energy and the activated complex in a reaction?
24. One way to determine the relationship between the reaction rate and the concentration is to determine the initial rates of reactions at different concentrations. Describe how this type of study is performed.
25. Each elementary step in a reaction mechanism usually occurs between two particles. Why is this important for each step in a reaction mechanism?
26. Name factors that would affect the ability of a substance to catalyze a reaction. How does each factor affect the catalytic process?
27. For a reaction at room temperature, a plot of the rate of reaction vs. concentration of reactant gives a straight line.
   a. How are the rate of reaction and concentration related?
   b. What does the slope of the graph of rate vs. concentration represent?
   c. What is the order of the reaction represented by this straight line relationship?
28. The rate law for the reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ is rate $= k[NO][O_2]$.
   a. If the concentration of each reactant is reduced by 50%, what will be the overall effect on the value of the rate constant?
   b. A proposed mechanism for the reaction has two steps:
   Step 1: $NO + O_2 \rightarrow NO_3$
   Step 2: $NO_3 + NO \rightarrow 2NO_2$
   What label is given to NO_3 in this reaction mechanism?

Thinking and Investigation

Use the potential energy diagram below to answer questions 29 to 35.



29. What is the $E_{a(fwd)}$ of the uncatalyzed reaction?
30. What is the $E_{a(fwd)}$ of the catalyzed reaction?
31. Which reaction is faster? Why?
32. What is the $E_{a(rev)}$ of the uncatalyzed reaction?
33. What is the $E_{a(rev)}$ of the catalyzed reaction?
34. What is the ΔH_r of the forward reaction?
35. What is the ΔH_r of the reverse reaction?
36. For the decomposition reaction $2AB \rightarrow A_2 + B_2$, the concentration of A_2 after 4.4 min = 0. 52 mol/L and after 5.6 min its concentration is 0.68 mol/L. What is the average rate of change in the concentration of AB over this period of time?
37. The reaction between copper and 1.0 L of nitric acid, $HNO_3(aq)$, is written as follows:
   $Cu(s) + 4HNO_3(aq) \rightarrow$
   $Cu(NO_3)_2(aq) + 2H_2O(\ell) + 2NO_2(g)$
   The concentration of the $HNO_3(aq)$ changes by 0.10 mol/L over a period of 1.5 min. What is the rate of change in the mass of the copper expressed in g/s?
38. Identify the potential energy diagram(s) that represent each of the following reactions. The reaction that
   a. has the largest $E_{a(fwd)}$
   b. has the smallest ΔH_r
   c. is endothermic
   d. occurs the fastest



39. Consider the following reaction:

$$4HBr(g) + O_2(g) \rightarrow 2Br_2(g) + 2HO(g)$$

Explain using words and an equation how the rate of decomposition of HBr (in mol/L·s) compares with the rate of formation of Br_2 (in mol/L·s).

40. Consider the following reaction:

$$MgCO_3(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(\ell) + CO_2(g)$$

It is determined that 0.48 g of $MgCO_3(s)$ reacts in 5.8 min. Calculate the rate at which $CO_2(g)$ is generated in moles per second.

41. Consider the following reaction:

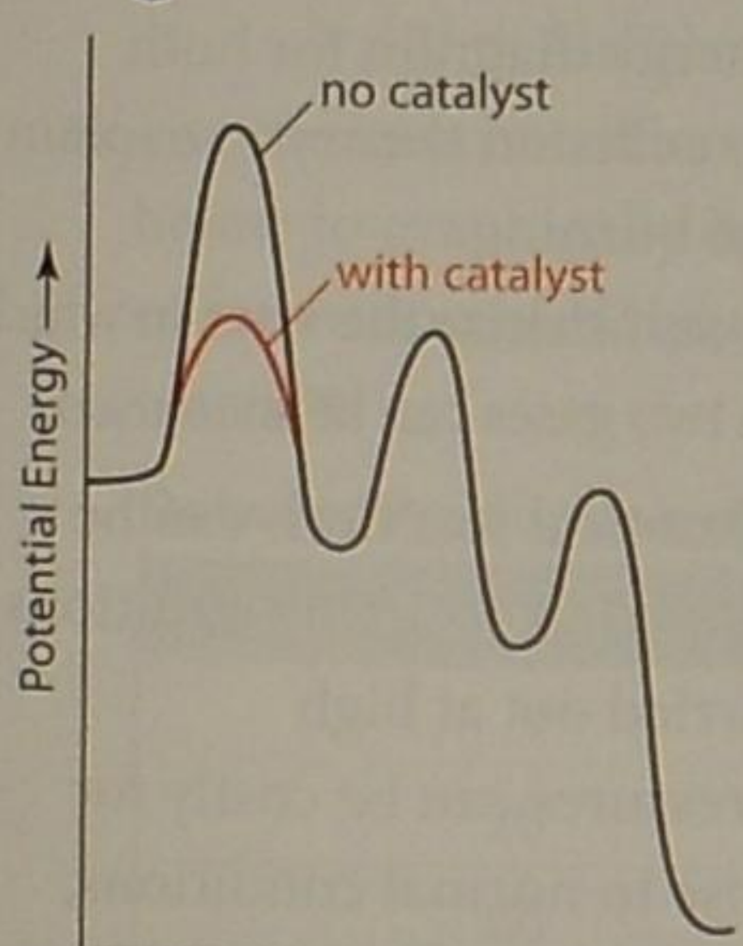
$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$

A proposed mechanism for this reaction is

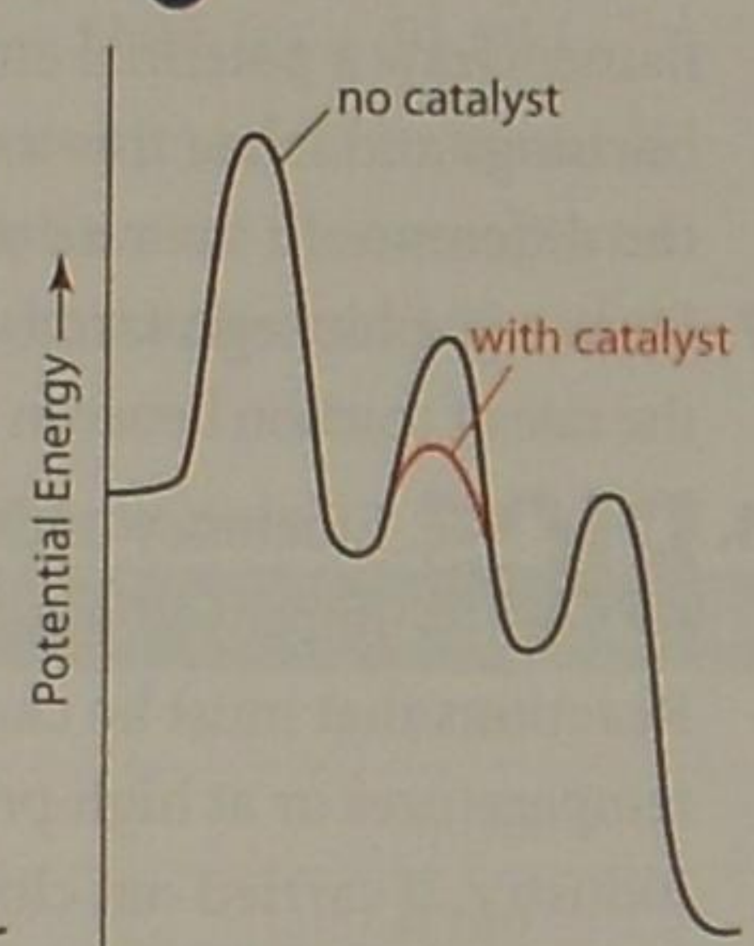
Step 1: $H_2 + NO \rightarrow H_2O + N$ (slow)
Step 2: $N + NO \rightarrow N_2 + O$ (fast)
Step 3: $O + H_2 \rightarrow H_2O$ (fast)

If a catalyst was used with this reaction, which potential energy diagram shown below would most accurately show the catalytic action on the mechanism? Explain why it would.

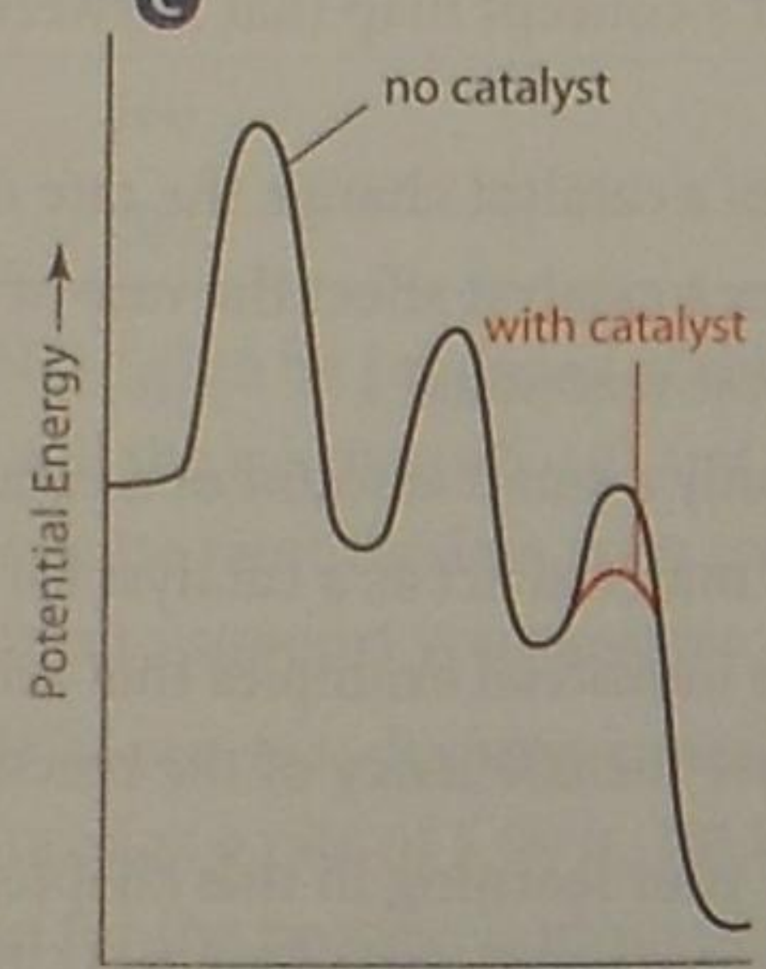
A



B



C

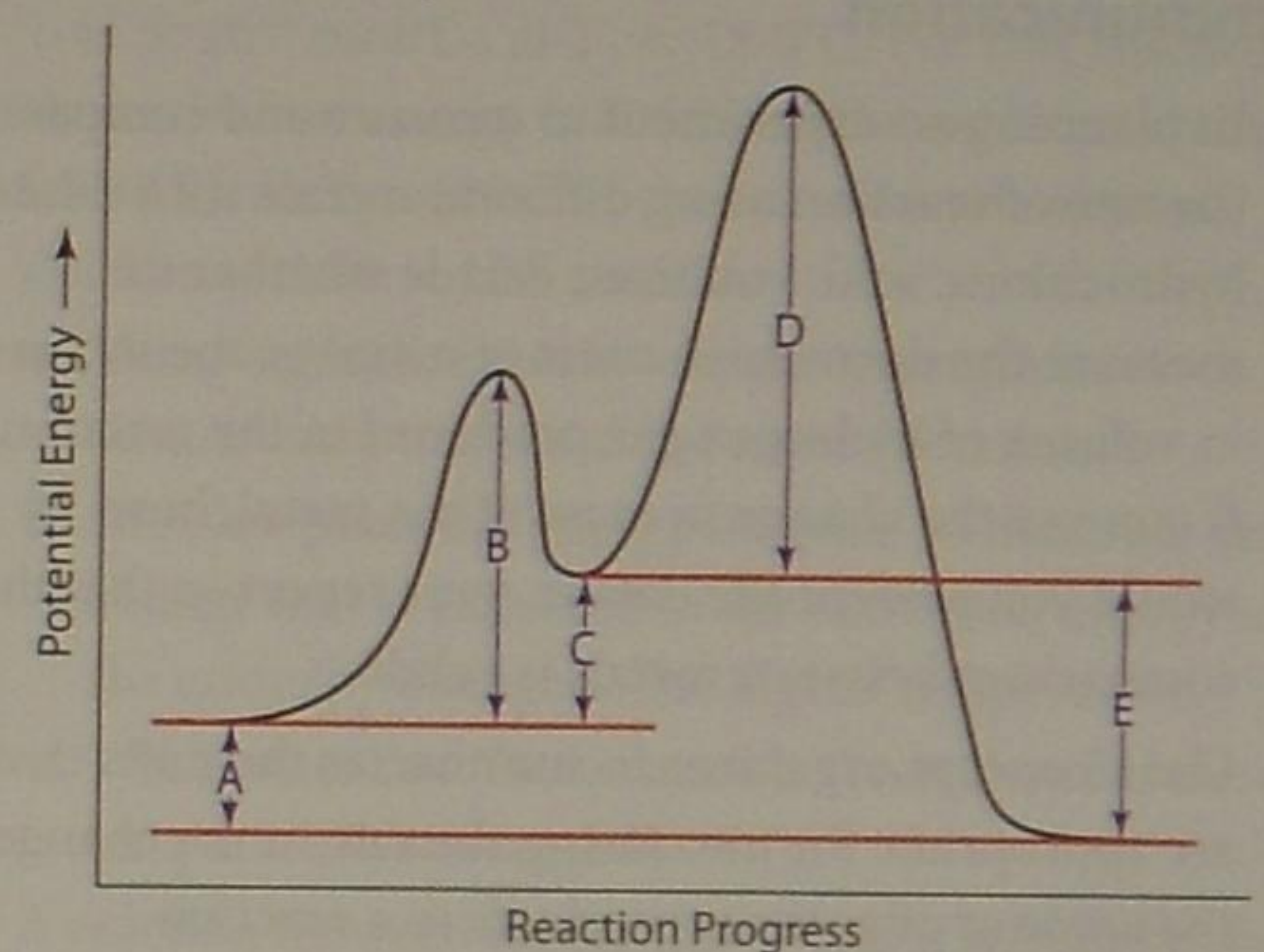


42. The enthalpy change, ΔH, for an endothermic reaction is +25 kJ. The activation energy for the forward reaction, $E_{a(fwd)}$, is +45 kJ.

a. What is the activation energy for the reverse reaction, $E_{a(rev)}$?

b. If the reaction was exothermic with an enthalpy of reaction of −25 kJ, and the forward reaction still had an activation energy of +45 kJ, would the reverse reaction have the same activation energy as in (a)? Show your reasoning with a calculation.

43. Examine the potential energy diagram shown below and answer the questions that follow.



a. How many steps are in this reaction?

b. What quantity would represent the overall activation energy for the reaction?

c. Is the overall reaction exothermic or endothermic?

d. What does the quantity B represent?

e. What does the quantity E represent?

44. The rate law for two reactions are compared. For reaction A, rate = $k[R]^2$, and for reaction B, rate = $k[R][S]$.

a. What is the overall order of each reaction?

b. What is the effect on each reaction of doubling the molar concentration of R?

45. Identify the role of each of the following in the reaction mechanism below.

a. P_2 **b.** PQ **c.** P_2Q_2 **d.** Q_2

Step 1: $P_2 + Q_2 \rightarrow 2PQ$
Step 2: $2PQ \rightarrow P_2Q_2$
Step 3: $P_2Q_2 \rightarrow P_2 + Z$

46. Two gases, $X_2(g)$ and $Y_2(g)$, react in a closed container. The rate law for the reaction is rate = $k[X_2]$. If the volume of the container is reduced to half the original volume, how will the rate be affected?

47. A mechanism has been proposed for the reaction below:

$$C_2H_5Br + C_6H_6 \rightarrow HBr + C_2H_5C_6H_6$$

Step 1: $C_2H_5B_r + AlBr_3 \rightarrow AlBr_4^- + C_2H_5^+$

Step 2: $C_2H_5^+ + C_6H_6 \rightarrow C_6H_6C_2H_5^+$ (slow)

Step 3: $C_6H_6C_2H_5^+ + AlBr_4^- \rightarrow AlBr_3 + HBr + C_2H_5C_6H_6$

a. Identify the rate-determining step.

b. Identify any intermediates that occur in this mechanism.

c. Is there a catalyst shown in this mechanism? Explain your answer.

Communication

48. In planning an experiment to measure and compare the rate of reaction using different metals with dilute hydrochloric acid, you must decide whether to measure the decrease in mass of metal or the increase in volume of hydrogen gas produced in the reaction. If you use the change in mass of the metal, how would you present the data in your report so that the comparison between metals is valid?

49. Use a concept organizer to summarize the units that are appropriate for measuring the rate in the change in the amount of gaseous products in a reaction.

50. The nature of activation energy is debated in your group. The statement that has been challenged is "*Activation energy depends on the frequency of collision between particles.*" Is this statement correct? Explain your reasoning.

51. Two measurements were made of a reaction to determine the instantaneous rate of reaction at different times. One measurement gave the rate of disappearance of reactants as 3.6×10^{-2} mol/L·s. Another measurement gave the rate of disappearance of reactants as 3.6×10^{2} mol/L·s. In your report of these results, explain how the two calculated instantaneous rates can be so widely different for the same reaction.

52. You are asked if a catalyst changes the rate of reaction in the same way that temperature changes the rate of reaction. How would you explain the difference?

53. The reaction between magnesium and dilute hydrochloric acid was used to illustrate the effect of surface area on the rate of reaction. In the first trial, the volume of hydrogen produced over 1 min was measured when a cube of magnesium having a known surface area reacted. The reaction was repeated using two identical cubes of magnesium, each with the same surface area as the cube used in the first trial. In this trial, twice as much hydrogen gas was collected in 1 min.

One person claims that the results demonstrate that the rate of reaction increases with an increase in surface area. Another person states that this is not a case of more surface area and the results do not illustrate the relationship between surface area and rate of reaction. Which person is correct? Give a reason for your answer, using a diagram to support your answer.

54. Two reactions occur at the same temperature and are between two reactants. Both reactions have an activation energy of +60 kJ but one is endothermic and the other is exothermic. Explain to someone in your class why the two reactions will not necessarily have the same rate of reaction.

55. Use a graphic organizer to summarize the factors to consider when selecting a catalyst for a reaction.

56. When demonstrating the effect of surface area on the rate of reaction, your instructor first ignites a pile of flour on a wire gauze pad and then blows powdered flour into a flame. The piled-up flour is not easily ignited and burns slowly. The flour blown into the flame ignites immediately and burns in a burst of flame. Draw a potential energy diagram for both burnings and relate this to collision theory to explain the difference in the rate of burning.

57. Draw a graphic organizer to summarize the ways in which the rate of reaction between two gases can be increased.

58. **BIG IDEAS** Efficiency of chemical reactions can be improved by applying optimal conditions. Reactions that must be carried out at high temperatures or at high pressures can be costly for industry. If carried out close to normal conditions, the reaction becomes more cost-efficient. The use of a catalyst can achieve this efficiency. Create a display or construct a concept map that answers the following questions:

a. How does a catalyst change the rate of a reaction?

b. How does a catalyst affect the rate of the forward and reverse reactions?

c. Why is only a small amount of a catalyst necessary?

d. Will any material act as a catalyst for a reaction?

e. Give two industrial examples that rely on a catalyst to increase the efficiency of the reaction.

59. Summarize your learning in this chapter using a graphic organizer. To help you, the Chapter 6 Summary lists Key Terms and Key Concepts. Refer to Using Graphic Organizers in Appendix A to help decide which graphic organizer to use.

Application

60. In the contact process to make sulfuric acid, sulfur dioxide, $SO_2(g)$, is needed. This gas can be made by heating pyrite, $FeS_2(s)$.

$$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

a. What would be an appropriate unit to measure the rate of decomposition of $FeS_2(s)$?

b. What would be an appropriate unit to measure the rate of formation of $SO_2(g)$?

c. How can the rate of decomposition of $FeS_2(s)$ and the rate of formation of $SO_2(g)$ be compared? How do the two rates compare?

61. In the Hall-Heroult process, molten cryolite, Na_3AlF_6, decomposes as shown by the equation below:

$$Na_3AlF_6(\ell) \rightarrow 3Na(\ell) + Al(\ell) + 3F_2(g)$$

If the average rate of formation of $F_2(g)$ is 0.85 mol/s, what is the average rate of decomposition of Na_3AlF_6, in grams per second?

62. **BIG IDEAS** Energy changes and rates of chemical reactions can be described quantitatively.

A company produces ammonia to make fertilizer using the combination reaction below:

$$N_2(g) + H_2(g) \rightarrow 2NH_3(g) + 91.8 \text{ kJ}$$

a. Use the concentration vs. time data in the table below to graphically determine the average rate of formation of $NH_3(g)$ over the first 130 s of the reaction.

Data for Production of Ammonia

Time (s)	Concentration (mol/L)
0	0.000
20	0.0500
60	0.100
90	0.125
130	0.125
160	0.160
200	0.160

b. For the $NH_3(g)$ to be produced at this rate in the process, will the reactants $N_2(g)$ and $H_2(g)$ be used up at this same rate? Explain your reasoning using calculations to support your answer.

63. In an industrial process, dinitrogen pentoxide, $N_2O_5(g)$, is used at a rate of 5.00×10^2 kg per hour. The equation for the process is given below:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

What is the rate at which $NO_2(g)$ is produced in moles per minute?

64. In the Haber-Bosch process, it is estimated that in the catalyzed reaction, often only 15% of the nitrogen and hydrogen convert to ammonia for one pass of the gases through the reactor. Suggest a reason why the percentage conversion is so low in the presence of a catalyst. What could be done to improve the conversion?

65. To increase the efficiency of production of a product, a manufacturer investigates the effect of temperature on the process. A suggestion is made by the chemist that the reaction temperature be increased. The rate of the reaction between two gases that occurs in one step is 1.43×10^{-3} mol/L·s at $T_1 = 18.0°C$. For this reaction, the activation energy is 20 kJ and the enthalpy change is −30 kJ. At $T_2 = 28.0°C$, the reaction rate almost doubles to 2.50×10^{-3} mol/L·s.

a. Using a graph, explain why the increase in temperature increased the rate of reaction.

b. Sketch a potential energy diagram to illustrate any change that is expected in the activation energy and the enthalpy change at the higher temperature.

c. What other cost factor must be considered if the temperature is changed?

66. A reaction between substances D and E is found to be first order with respect to both D and E. Examine two proposed mechanisms for this reaction and explain which is more likely to be correct. Can it be stated with certainty that either of these mechanisms is correct? Explain your answer.

Mechanism 1

Step 1: $D \rightarrow G + H$ (slow)

Step 2: $E + G \rightarrow I$ (fast)

Mechanism 2

Step 1: $D + E \rightarrow DE$ (slow)

Step 2: $DE \rightarrow H + I$ (fast)

67. In an industrial process that is highly exothermic, a new, less costly, compound is to be substituted for an existing reactant. However, the process is difficult to initiate with the new material. Suggest a reason that may explain this difficulty in starting up the reaction. What other change could be introduced to allow the new reactant to be used?

68. Transition metals are frequently used as catalysts for industrial reactions. Use your knowledge of atomic structure to suggest why this type of metal is a good choice for a catalyst.

69. For what type of reaction is the number of collisions between reactants not a factor? Give an example.

Select the letter of the best answer below.

1. K/U Consider the reaction shown below:
$Mg(s) + 2CH_3COOH(aq) \rightarrow$
$Mg(CH_3COO)_2(aq) + H_2(g)$
The rate of reaction can be calculated over a period of time by determining the change in the
   a. pH of the solution.
   b. concentration of Mg(s).
   c. colour.
   d. temperature.
   e. volume of the solution.

2. T/I Reactant A(g) has a concentration of 0.39 mol/L at the beginning of a reaction. After 3.2 min the concentration of A(g) is 0.023 mol/L. What is the average rate of change of A(g) over this time?
   a. $5.0 \times 10^{-2} \frac{mol}{L \cdot s}$
   b. $1.1 \times 10^{-1} \frac{mol}{L \cdot s}$
   c. $3.9 \times 10^{-1} \frac{mol}{L \cdot s}$
   d. $3.9 \times 10^{-2} \frac{mol}{L \cdot s}$
   e. $1.9 \times 10^{-3} \frac{mol}{L \cdot s}$

3. K/U For a reaction in aqueous solution, an increase in the concentration of the reactant(s) increases the rate of reaction because
   a. the potential energy of the chemical bonds is decreased.
   b. there are more collisions between reactant particles.
   c. the intermolecular attractions between water and the aqueous ions increase.
   d. the kinetic energy of the reactant particles increases.
   e. a greater percentage of the aqueous ions have energy equal to or in excess of the activation energy.

4. K/U Consider the potential energy diagram in question 23. Which of the following is the activation energy for the forward reaction in step 2?
   a. B
   b. H
   c. I
   d. J
   e. E

5. K/U The rate law expression for a reaction is rate $= k[B]^0[C]$. Based on this rate law, which statement is correct?
   a. The reaction is zero order overall.
   b. The reaction is second order overall.
   c. The reaction is first order with respect to B and C.
   d. The reaction is first order overall.
   e. The rate determining step must involve B.

6. T/I For a reaction having $\Delta H_r = +58$ kJ, the activation energy for the forward reaction, $E_{a(fwd)}$, is +89 kJ. What is $E_{a(rev)}$?
   a. +114 kJ
   b. +37 kJ
   c. +73 kJ
   d. −89 kJ
   e. +31 kJ

7. T/I Given the reaction mechanism shown below, for which substance would a change in concentration have the greatest effect on the overall rate of reaction?
Step 1: $A \rightarrow B + C$ (fast)
Step 2: $C + D \rightarrow F$ (slow)
Step 3: $F + B \rightarrow G$ (fast)
   a. A
   b. A + B
   c. D
   d. C + D
   e. F

8. K/U For any chemical reaction, which of the following is most closely related to the overall rate?
   a. the average rate of all the steps in the reaction mechanism
   b. the number of steps in the reaction mechanism
   c. the overall reaction
   d. the slowest step in the reaction mechanism
   e. the fastest step in the reaction mechanism

9. A A reaction mechanism is suggested for an industrial process.
Step 1: $A_2 \rightarrow 2A$ (slow)
Step 2: $2A + B \rightarrow C + D$ (fast)
Step 3: $D + G \rightarrow DG$ (fast)
Step 4: $DG \rightarrow F + G$ (fast)
Which statement about this mechanism is false?
   a. G is a catalyst.
   b. There will be four transitional states in this mechanism.
   c. Step 1 is the rate-determining step.
   d. There are two reaction intermediates in this mechanism.
   e. The overall reaction is $A_2 + B \rightarrow C + F$.

10. K/U Which property listed below does not apply to a catalyst?
   a. lowers the overall activation energy of a reaction
   b. increases the number of collisions
   c. reacts in one step but is regenerated in another step
   d. provides an alternate path for the reaction
   e. increases the rate of the rate-determining step in a reaction mechanism

Use sentences and diagrams as appropriate, to answer the questions below.

11. **K/U** For a reaction that is endothermic,
    a. how is $E_{a(fwd)}$ related to $E_{a(rev)}$ and ΔH_r?
    b. how do $E_{a(fwd)}$ and $E_{a(rev)}$ compare in magnitude?

12. **C** A reaction between two gases occurs in a closed container that is fitted with a piston that can be moved to adjust the total volume. Explain how you would use diagrams of the apparatus to explain to a group how the rate of reaction between the gases increases with a decrease in volume.

13. **A** A company is testing potassium chlorate as an accelerant in the manufacture of a firecracker.

$$2KClO_3(s) + \text{heat} \rightarrow 2KCl(s) + 3O_2(g)$$

If 0.20 g of $KClO_3(s)$ decomposes in 2.8 s, at what rate is oxygen, $O_2(g)$, released over this time at SATP?

14. **A** A box is labelled *Explosives*, yet it does not explode. Explain why.

15. **C** Prepare a graphic presentation that illustrates to the class how collision theory can account for a doubling of the rate of reaction when the temperature increases by 20°C.

16. **T/I** Sketch a potential energy diagram based on the data below and determine the overall enthalpy change for the reaction.

Step 1: $E_{a(fwd)} = +11$ kJ, $E_{a(rev)} = +31$ kJ

Step 2: $E_{a(fwd)} = +61$ kJ, $\Delta H_{fwd} = +31$ kJ

Step 3: $E_{a(fwd)} = +31$ kJ, $\Delta H_{fwd} = -75$ kJ

17. **A** For the reaction shown below, it was determined by experiment that nitrous oxide, NO(g), was reacting at an initial rate of 0.050 mol/L·s. Was $H_2O(g)$ used up at an equal rate? Explain your reasoning.

$$4NO(g) + 6H_2O(g) \rightarrow 4NH_3(g) + 5O_2(g)$$

18. **C** The following reaction is known to be second order with respect to $NO_2(g)$ and zero order with respect to CO(g). Propose a mechanism for this reaction.

$$NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$$

19. **T/I** Consider the following reaction:

$$2AgNO_3(aq) + CuCl_2(aq) \rightarrow 2AgCl(s) + Cu(NO_3)_2\,(aq)$$

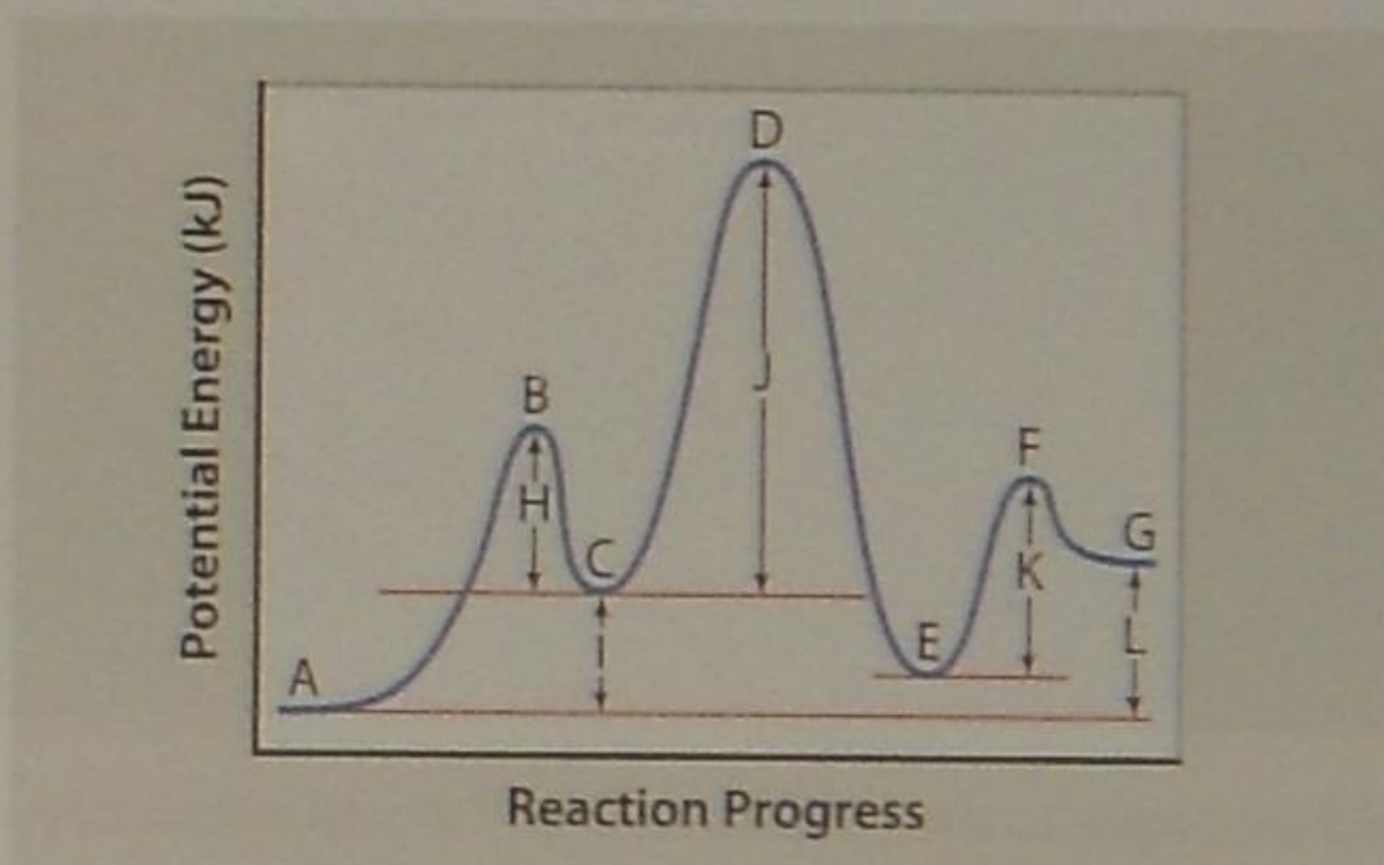
The concentration of $Ag(NO_3)_2(aq)$ at $t = 30.0$ s is 0.42 mol/L. At $t = 60.0$ s its concentration is 0.28 mol/L. What is the change in $[Cl^-]$ during this time?

20. **T/I** An exothermic reaction carried out at 10°C has an activation energy of +65 kJ and enthalpy change $\Delta H_r = -80$ kJ. How would these two properties change when the concentration of the reactants are altered to double the rate of reaction? Explain your answer.

21. **K/U** A second-order reaction follows the rate law rate $= k[Br_2]^2$. Is this a first-order or second-order reaction? Explain your answer.

22. **T/I** A reaction produces 0.20 mol/L of product per minute at 25°C. Explain how you could get the same reaction to produce 0.50 mol/L of product per minute without changing the contents of the reaction vessel.

23. **K/U** Examine the potential energy diagram for a reaction mechanism and answer the questions that follow.



a. How many steps are involved? Explain.
b. Identify each label in this potential energy diagram.
c. Overall, is a net amount of energy added or released?

24. **A** Explain what femtosecond technology is and how it is used to study reaction mechanisms.

25. **C** Explain how an increase in temperature affects the rate of a reaction. Sketch a graph to use as the basis for your explanation.

Self-Check

If you missed question ...	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Review section(s)...	6.1	6.1	6.2	6.2	6.3	6.2	6.3	6.3	6.3	6.2	6.2	6.2	6.1	6.2	6.2	6.2	6.3	6.3	6.1	6.2	6.3	6.2	6.2	6.3	6.2

Conduct an Inquiry

Neutralizing a Sulfuric Acid Spill

In 2007, a train derailment caused approximately 150 000 L of sulfuric acid to spill into a tributary of the Blanche River just north of North Bay, Ontario. Sulfuric acid has many applications in chemical industries, including the manufacture of paper, soap, and batteries. It is highly corrosive and its fumes are extremely harmful if inhaled. Numerous organisms were harmed as a result of the North Bay spill because the pH of the river water had dropped significantly before workers were able to neutralize the acid. Sulfuric acid also undergoes a violent exothermic reaction when mixed with water. The resulting change in water temperature may have harmed organisms as well.

In this project, you will assume the role of a hazardous materials consultant who is hired by the Ontario government to determine the most suitable method for neutralizing a sulfuric acid spill in a river. You will experimentally determine the temperature change that occurs when sulfuric acid is added to water. Then you will determine the suitability of various neutralizing agents, taking into account several factors, including the change in river water temperature after each neutralization reaction. Finally, you will present your findings and recommendation to the government.

Which neutralizing agent is the most suitable for neutralizing a sulfuric acid spill in a river?

A rapid response to the sulfuric acid spill in a tributary of the Blanche River near North Bay, Ontario in 2007 helped to reduce environmental damage. This response included adding a neutralizing agent to the river water.

Initiate and Plan

1. Use print and Internet resources to research factors that will help you evaluate which neutralizing agent is the most suitable for neutralizing sulfuric acid that has spilled into a river. The neutralizing agents you will consider are calcium carbonate, $CaCO_3(s)$; sodium carbonate, $Na_2CO_3(s)$; sodium hydrogen carbonate, $NaHCO_3(s)$; and calcium oxide, $CaO(s)$.
   - What terms, such as *thermal pollution*, do you need to define to better understand the scientific material you are reading?
   - How can a change in water temperature affect aquatic ecosystems?
   - What other factors, such as cost, might affect the suitability of a neutralizing agent?
2. Design an investigation that uses a simple calorimeter to measure the temperature change that occurs when sulfuric acid is added to water.
   - Write a brief overview of your experimental design.
   - Draw a diagram of the calorimeter you will use, labelling its components clearly.
   - List the chemicals and equipment you will need. You will be using a dilution of concentrated sulfuric acid that is approved for use in a school laboratory.
   - Describe all necessary safety precautions. Refer to any relevant material safety data sheets (MSDS) to explain why you must use a dilution of concentrated sulfuric acid in your investigation.
   - Write a step-by-step procedure for your investigation.
3. Have your teacher approve your experimental design, materials, procedure, and safety precautions.

Perform and Record

4. Conduct your investigation, repeating it at least once.
5. Use a table to record measurements and observations.

Analyze and Interpret

1. Your teacher will provide you with the temperature change that occurs when concentrated sulfuric acid is added to water. Compare and contrast this temperature change with the temperature change you measured in your investigation.

2. Use the temperature change for concentrated sulfuric acid to calculate the temperature of the river water immediately after the acid spill. Create a table to summarize your calculations.
   - Assume that the initial temperature of the river water was 10°C.
   - Assume that the area of river water affected by the acid spill was approximately 15 m wide, 500 m long, and 10 m deep.
   - Assume that the specific heat capacities of the sulfuric acid solution and the water are the same.
   - Use the following density values: 1 g/mL for the density of water, and 1.84 g/mL for the density of the concentrated sulfuric acid.

3. Write balanced equations for the reaction of sulfuric acid with each of the neutralizing agents below. (**Hint:** Assume that the products are a solid salt, liquid water, and carbon dioxide gas for all reactants except for (d).)

   a. $CaCO_3(s)$
   b. $Na_2CO_3(s)$
   c. $NaHCO_3(s)$
   d. $CaO(s)$

4. Calculate the enthalpy of reaction for the neutralization of sulfuric acid with each of the four reactants. Then use these values and the temperature of the river water immediately after the acid spill to calculate the temperature of the river water after each neutralization reaction. Create a table summarizing your calculations for each neutralization reaction. The following tips will help you complete your calculations.
   - Use Hess's law and standard molar enthalpies of formation to determine the enthalpy of reaction for each neutralization reaction. To complete your calculations, use the table "Selected Standard Molar Enthalpies of Formation" in Appendix B, as well as additional values provided by your teacher.
   - Calculate the temperature change and the final temperature of the river water after each neutralization reaction. Assume that this water includes both the water in the river and the water produced in the neutralization reaction. Also assume that the heat produced by each reaction is absorbed by both sources of water.

5. Use your research and calculations to evaluate which reaction is the most suitable for neutralizing sulfuric acid. Explain your reasoning.

Communicate Your Findings

6. Decide on the best way to present your findings and recommendation to the government, such as a computer presentation, a written report, or an interactive Web page.

7. Prepare a presentation that includes the following:
   - a summary of your experimental design and results
   - tables summarizing the calculations you performed
   - your evaluation of the most suitable method for neutralizing a sulfuric acid spill in a river and an explanation of the factors you took into account
   - a literature citation section that documents the sources you used to complete your research, using an appropriate academic format

Assessment Criteria

Once you complete your project, ask yourself these questions. Did you…

- ☑ **T/I** assess your information sources for accuracy and reliability?
- ☑ **K/U** describe your experimental design, including any safety precautions?
- ☑ **T/I** conduct your investigation, repeating your procedure at least once?
- ☑ **C** use tables to record your measurements and calculations?
- ☑ **A** use your research and calculations to evaluate which reaction is the most suitable for neutralizing a sulfuric acid spill in a river?
- ☑ **C** communicate your findings in a format that is appropriate to your audience and purpose, using suitable instructional visuals and scientific vocabulary?
- ☑ **C** document your sources using an appropriate academic format?

UNIT 3 SUMMARY

BIG IDEAS

- Energy changes and rates of chemical reactions can be described quantitatively.
- Efficiency of chemical reactions can be improved by applying optimal conditions.
- Technologies that transform energy can have societal and environmental costs and benefits.

Overall Expectations

In this unit, you learned how to…

- **analyze** technologies and chemical processes that are based on energy changes, and **evaluate** them in terms of their efficiencies and their effects on the environment
- **investigate** and **analyze** energy changes and rates of reaction in physical and chemical processes, and **solve** related problems
- **demonstrate** an understanding of energy changes and rates of reaction

Chapter 5 Energy Changes

Key ideas

- A system is the object or substance being studied, and the surroundings are everything else in the universe. Systems can be open, closed, or isolated.
- The first law of thermodynamics states that energy cannot be created or destroyed but can be transformed from one type of energy to another type of energy or transferred from one object to another object.
- The second law of thermodynamics states that, when two objects are in thermal contact, heat will be transferred from the object at a higher temperature to the object at the lower temperature until they reach thermal equilibrium.
- An enthalpy change in a system, occurring at constant pressure, is the same as the amount of heat that is exchanged between the system and its surroundings. Enthalpy changes can be positive or negative and depend only on the initial and final states of the system.
- The standard enthalpy of a reaction as written, ΔH_r°, is the enthalpy change for the amount in moles of each reactant and product as determined by the coefficients in the chemical equation.
- A process taking place in a simple calorimeter occurs at constant pressure. The amount of heat that is exchanged between the calorimeter and the system is equal to the change in the enthalpy of the system.
- Hess's law states that the enthalpy change of a physical or chemical process depends only on the initial and final conditions. The enthalpy change of the overall process is the sum of the enthalpy changes of its individual steps.

- The standard enthalpy of formation of a compound, ΔH_f°, is the enthalpy change that results from synthesizing 1 mol of the compound from its elements in their most stable state under standard conditions.
- You can calculate the enthalpy change for any reaction by applying the formula

$$\Delta H_r^\circ = \Sigma(n\Delta H_f^\circ \text{ products}) - \Sigma(n\Delta H_f^\circ \text{ reactants})$$

- The efficiency of a chemical, physical, or nuclear process can be expressed as

$$\text{efficiency} = \frac{\text{energy output}}{\text{energy input}} \times 100\%$$

- Fossil fuels are non-renewable resources, which contribute to global warming, acid rain, and pollution of the environment. Renewable energy resources include hydroelectric power, solar energy, and wind energy.

Chapter 6 Rates of Reaction

Key ideas

- A reaction rate is the speed at which a chemical reaction occurs. A reaction rate is measured by the change in the amount of reactants consumed or products formed over a given time interval.
- The instantaneous rate of a reaction is the rate of the reaction at a particular point in time.
- The average rate of a chemical reaction is the change in the concentration of a reactant or a product per unit time over a given time interval.
- According to collision theory, a reaction will occur only if the reactants collide with the correct orientation and with energy equal to or above the activation energy, E_a.

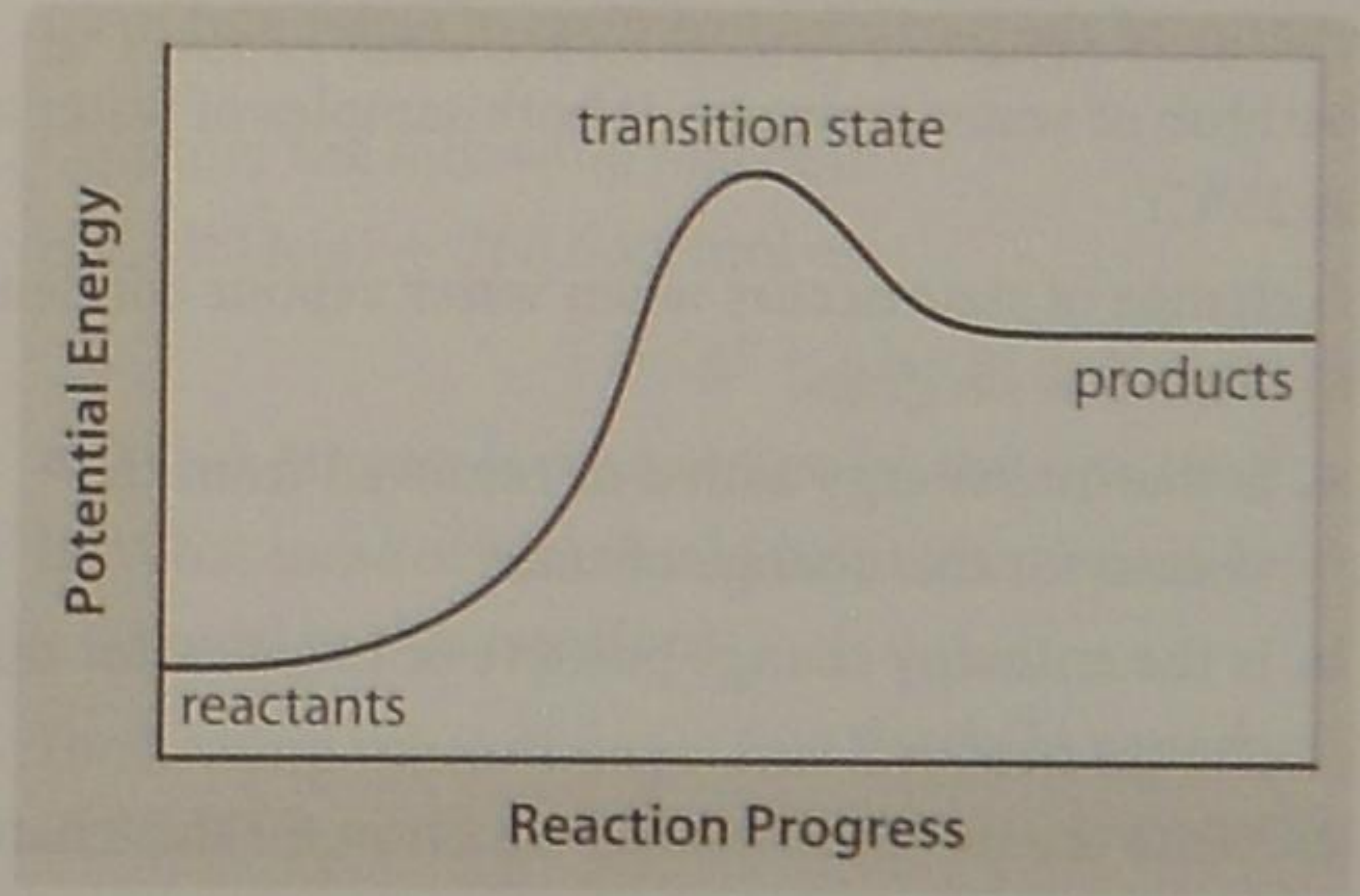
- When reactants collide with sufficient energy to overcome the activation energy barrier, they form an activated complex, which is an unstable transition state.

- Factors that affect the rate of a chemical reaction include the nature of the reactants, the concentration of a solution, the temperature, the pressure of gaseous reactants, the surface area of solid particles of the reactants, and the presence of a catalyst.
- A catalyst is a substance that increases the rate of a reaction but is itself unchanged at the end of the reaction.
- To determine the relationship between the rate of a reaction and the concentration of reactants, several experiments must be carried out and the initial rates of each reaction determined.
- The rate of a reaction can be directly proportional to the concentration of a reactant, or proportional to the square of the concentration of a reactant.
- The rate law for a chemical reaction is a mathematical relationship that must be determined experimentally.
- Elementary steps are a series of simple reactions that describe the progress of an overall reaction at the molecular level.
- The slowest elementary step in a chemical reaction determines the rate of the overall reaction.

Knowledge and Understanding

Select the letter of the best answer below.

1. The total kinetic energy of all the particles in a sample represents the ____________ of a sample.
   a. thermal energy
   b. potential energy
   c. enthalpy of formation
   d. activation energy
   e. enthalpy
2. Which source of energy for production of electricity has the least negative impact on the environment?
   a. coal
   b. natural gas
   c. oil
   d. solar
   e. propane
3. A match is not needed to keep a fire burning because the
   a. reaction is endothermic and heat energy is constantly absorbed.
   b. heat dissipates quickly.
   c. reaction is exothermic and the heat given off is used to supply kinetic energy to the fuel.
   d. oxygen provides thermal energy to maintain the reaction.
   e. heat from the match lowers the activation energy.
4. A kettle uses 925 kJ of electrical energy to heat a given mass of water by 40.0°C. In terms of energy efficiency, what does this quantity of energy represent?
   a. energy input
   b. the minimum efficiency
   c. the EnerGuide rating
   d. the maximum efficiency
   e. energy output
5. The total enthalpy of the reactants in a reaction is 300 kJ and the total enthalpy of the products is 250 kJ. Which statement about the reaction is correct?
   a. The reaction cannot occur.
   b. The ΔH is 300 kJ.
   c. The reaction is exothermic.
   d. The thermal energy given off is 550 kJ.
   e. The energy needed to break the bonds in the reactants is 550 kJ.
6. Which factor will not affect the rate of the reaction shown below?
   $$Ca(s) + H_2O(\ell) \rightarrow Ca(OH)_2(aq) + H_2(g)$$
   a. use of a catalyst
   b. increase in pressure
   c. increase in surface area of Ca(s)
   d. increase in water temperature
   e. decrease in water temperature
7. Which of the following statements about the chemical reaction represented by the potential energy diagram below is correct?



   a. The forward reaction is exothermic.
   b. $E_{a(fwd)}$ is less than $E_{a(rev)}$.
   c. ΔH_{rev} is a positive quantity.
   d. ΔH_{fwd} is a negative quantity.
   e. ΔH_{rev} is equal in magnitude to ΔH_{fwd}.

8. Which of the following represents the units for the rate constant for a reaction that is second order in one reactant and zero order in another reactant?
   a. mol·s/L^2
   b. mol^2·s/L^2
   c. L·s/mol
   d. L/mol·s
   e. L/mol^2·s

9. What is the overall order of reaction for a chemical reaction that has the following rate law:
   rate = $k[A]^1[B]^0$
   a. 0
   b. 1
   c. 2
   d. 3
   e. cannot be determined

10. Which statement is predicted by collision theory?
    a. Twice as many collisions result in twice the rate of reaction.
    b. All collisions between particles with kinetic energy equal to the activation energy lead to product formation.
    c. Collisions between particles at a favourable orientation, but with energy less than the activation energy, are effective.
    d. The kinetic energy of at least one of the reactants must equal the potential energy of the activated complex.
    e. Only collisions between particles at the correct orientation and with kinetic energy equal to or in excess of the activation energy can lead to product formation.

Answer the questions below.

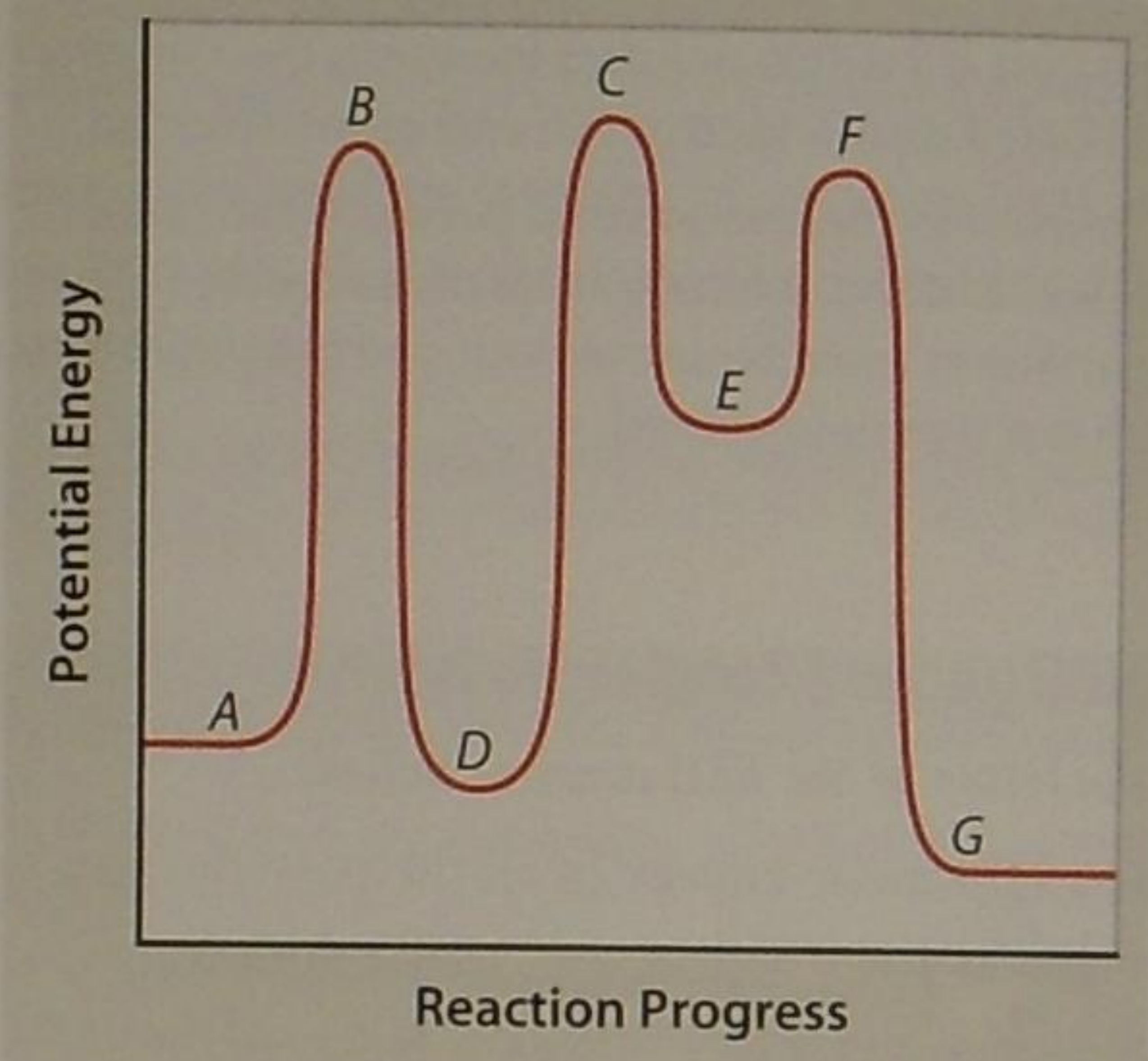
11. How do the average kinetic energy and the thermal energy of the particles in a glass of water and in a bathtub of water compare, if both samples of water are at 25°C?

12. A change of state occurs when water vapour condenses to form dew on grass.
    a. Is thermal energy added or removed from the system for this change of state?
    b. Is the enthalpy change positive or negative for this change of state?
    c. Write the thermochemical equation for this change of state. Refer to **Table 5.2**.

13. Define the term *activation energy*, E_a. What is the main factor that affects the magnitude of the activation energy for a reaction?

14. Does the magnitude of the activation energy for a reaction depend upon whether or not the reaction is endothermic or exothermic? Explain your answer.

15. K/U Examine the potential energy diagram below.



    a. How many steps are represented in this energy diagram? Give a reason for your answer.
    b. For which step does the enthalpy change have the greatest magnitude?
    c. The difference between which two letters represents the activation energy for the reverse of step 2?
    d. Which letters correspond to transition states?
    e. What does the energy between E and F represent?

16. Consider the following reaction:
    $2HCl(aq) + LiCO_3(s) \rightarrow 2LiCl(aq) + CO_2(g) + H_2O(\ell)$
    a. What quantities could be measured to determine the average rate of reaction?
    b. Would the instantaneous rate be determined in the same way? Give a reason for your answer.

17. The rate of a particular reaction between two gases was found to double when the temperature was increased. How do collision theory and kinetic molecular theory explain this change in reaction rate?

18. Several industrial catalysts are listed below. Copy the chart into your notebook and complete it by providing the names of the products for the applications. Where applicable, also name the industrial process.

Applications of Some Catalysts

Catalyst	Product	Process
Fe, K_2O, Al_2O_3		
V_2O_5		
Pt/Ir		
Xylanase		
Amylase		

19. How does a catalyst change the rate of a reaction?

20. A reaction mechanism is a proposed series of elementary steps that describe the progress of a reaction.
   a. What is an elementary step?
   b. What is the rate-determining elementary step?
   c. With respect to potential energy, what is a consistent characteristic of the rate-determining step in the reaction?
   d. How is the rate-determining step related to the rate law for the overall reaction?

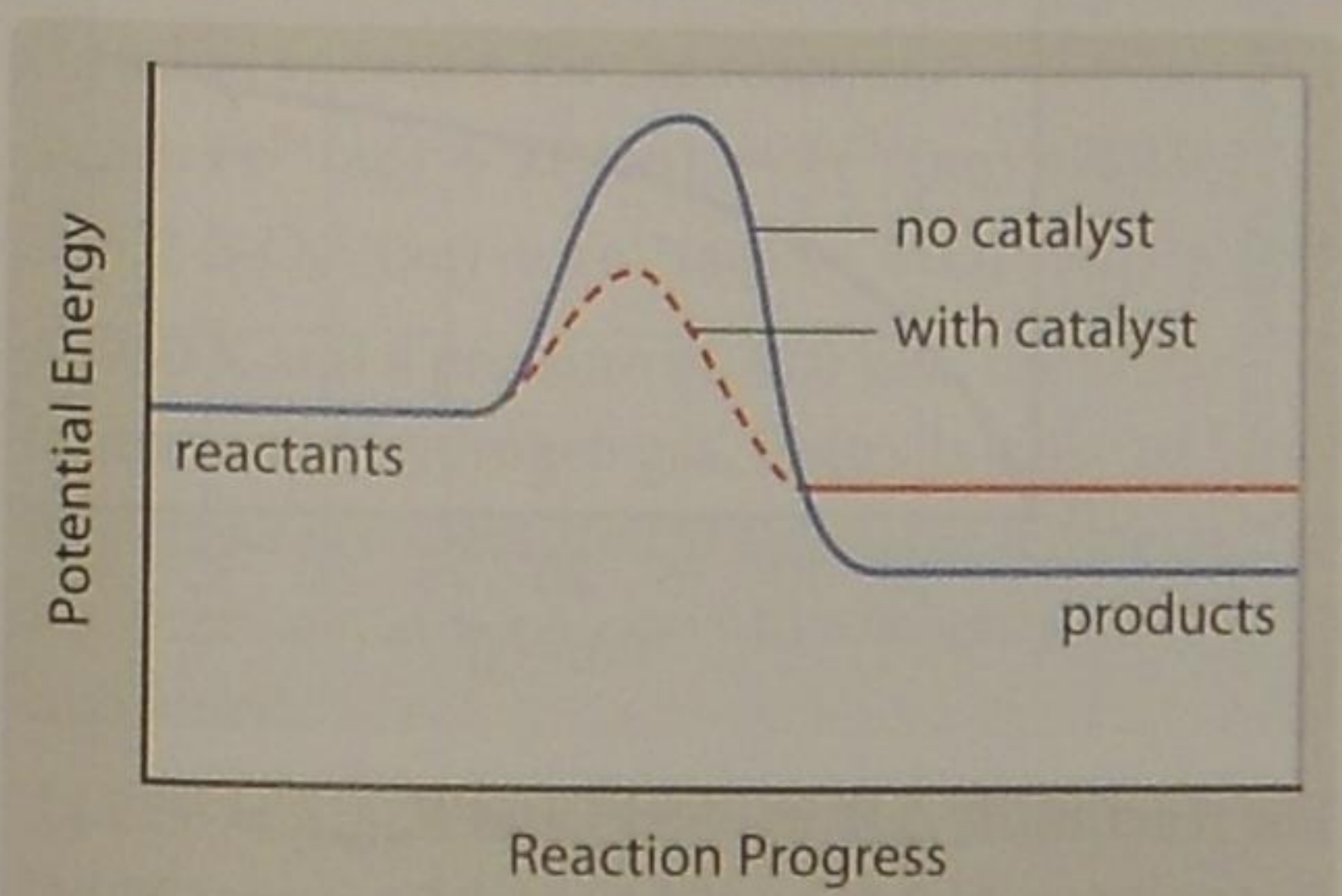
21. What information can be learned from knowing the rate constant, k, for a reaction?

22. Is a measurement of temperature change an effective way to monitor the rate of reaction for reactions in aqueous solution? Give a reason for your answer.

23. An exothermic and an endothermic reaction both have the same high value for E_a. Can it be stated that this indicates that over the same period of time, the average rate of reaction for each reaction would be the same? Explain your reasoning.

24. A 10°C increase in temperature will almost double the rate of reaction for many reactions between gases. This is not true for reactions in aqueous solution. Explain the reason for this difference.

25. Potential energy diagrams for a reaction with and without a catalyst are shown below. Is the information shown possible? Give a reason for your answer.



Thinking and Investigation

26. The standard molar enthalpy of formation, ΔH_f°, for ozone, $O_3(g)$, is +142.7 kJ/mol. What is the enthalpy of reaction for the reaction below?
   $2O_3(g) \rightarrow 3O_2(g)$

27. Use the enthalpy changes given below to write the thermochemical equation for each reaction.
   a. Dissolving of ammonium nitrate, $NH_4NO_3(s)$, $\Delta H_{solution} = +25.69$ kJ/mol
   b. Complete combustion of 1-pentanol, $C_5H_{11}OH(\ell)$, $\Delta H^\circ_{comb} = -3330.9$ kJ/mol
   c. Enthalpy of formation for phenol, $C_6H_5OH(s)$, $\Delta H_f^\circ = -164.9$ kJ/mol

28. Ammonia, $NH_3(s)$, melts at −78°C. This change of state can be represented by the following equation:
   $$NH_3(s) + 5.66\text{ kJ} \rightarrow NH_3(\ell)$$
   What amount of heat is given off when 6.46 g of $NH_3(\ell)$ solidifies?

29. Refer to the data for methane, $CH_4(g)$, in **Table 5.2**.
   a. Write the thermochemical equation for the condensation of methane.
   b. What amount of thermal energy is absorbed by 100.0 g of methane when it changes from a liquid to a gas?

30. The enthalpy change for the following reaction, as written, is −906 kJ.
   $$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$
   What is the molar enthalpy change for each reactant and product?

31. What is the final temperature of a 324 g sample of liquid that has a specific heat capacity of 2.8 J/g·°C when it absorbs 2.56 kJ of thermal energy? The initial temperature of the liquid is 5.0°C.

32. An experiment indicates that the burning of 0.26 mol of a fuel emitted 355.4 kJ of thermal energy.
   a. What is the molar enthalpy of combustion of the fuel?
   b. Refer to **Table 5.4** to identify the fuel.

33. Consider the following reaction:
   $$NH_4HSO_3(s) + 768.6\text{ kJ/mol} \rightarrow \tfrac{5}{2}H_2(g) + \tfrac{1}{2}N_2(g) + S(s) + \tfrac{3}{2}O_2(g)$$
   a. What process is represented by the equation?
   b. What mass of S(s) would be formed when 2690.1 kJ is used in this reaction?

34. The heating value of diesel fuel has been reported as 44.80 MJ/kg, and for gasoline the value is 47.30 MJ/kg, assuming that the products of combustion are $CO_2(g)$ and $H_2O(\ell)$. How much more water, expressed in kilograms, could be converted to steam at 100°C by heating with 1.00 kg of gasoline rather than 1.00 kg of diesel fuel? Refer to **Table 5.2** for additional data to perform this calculation.

35. For which of the following reactions will the enthalpy of reaction be a negative value?

a. sulfur burning in a crucible

b. NaI(s) dissolving in water, causing the temperature to increase

c. the process of photosynthesis, where $CO_2(g)$ and $H_2O(\ell)$ combine in the presence of sunlight to form glucose and $O_2(g)$

d. adding concentrated sulfuric acid to water, causing the temperature to increase from 15°C to 75°C

e. iron rusting

f. $CO_2(g) \rightarrow CO_2(s)$

g. $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

36. A methanol lamp is used to heat 500.0 g of water. When 1.84 g of methanol is burned, the temperature of the water increases from 18.4°C to 30.7°C.

a. What amount of thermal energy did the water gain?

b. Use the data for the molar enthalpy of combustion of methanol, $CH_3OH(\ell)$, from **Table 5.4** to determine the amount of thermal energy given off during the burning.

c. Identify the energy input and the energy output for this system.

d. Calculate the efficiency of the methanol lamp as it heated the water.

37. Ethylene glycol, $C_2H_6O_2(\ell)$, has a range of uses from antifreeze in cooling and heating systems and deicer of airport runways and aircraft to the formulations of printers' inks and inks for ballpoint pens. The complete combustion of this compound is shown below.

$$C_2H_6O_2(\ell) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell) + 1190 \text{ kJ}$$

Use this information and the enthalpy of formation data in Appendix B to calculate the enthalpy of formation of ethylene glycol.

38. The enthalpy of combustion of natural gas is found to be 54.0 kJ/g. Refer to **Table 5.7** for the emission levels of fossil fuels. When 1.00 kg of natural gas is burned, what mass of particulate matter is released into the atmosphere?

39. Use the given equations to determine the enthalpy change for the reaction below:

$$2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$$

(1) $S(s) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H^\circ_{comb} = -296.8 \text{ kJ}$

(2) $S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g) \qquad \Delta H^\circ_{comb} = -395.7 \text{ kJ}$

40. The enthalpy of combustion of sucrose, $C_{12}H_{22}O_{11}(s)$, is −5650 kJ/mol. A 3.00 g sample of this sugar is burned in 38.0 s in a bomb calorimeter that has a heat capacity of 1284 J/°C.

a. What amount of heat will be given off during the burning?

b. What amount of heat will the calorimeter absorb?

c. By how much will the temperature of the calorimeter increase?

d. Express the rate of burning of sucrose, in moles per second.

41. Fe(s) will displace Ag^+ from solution, according to the equation below:

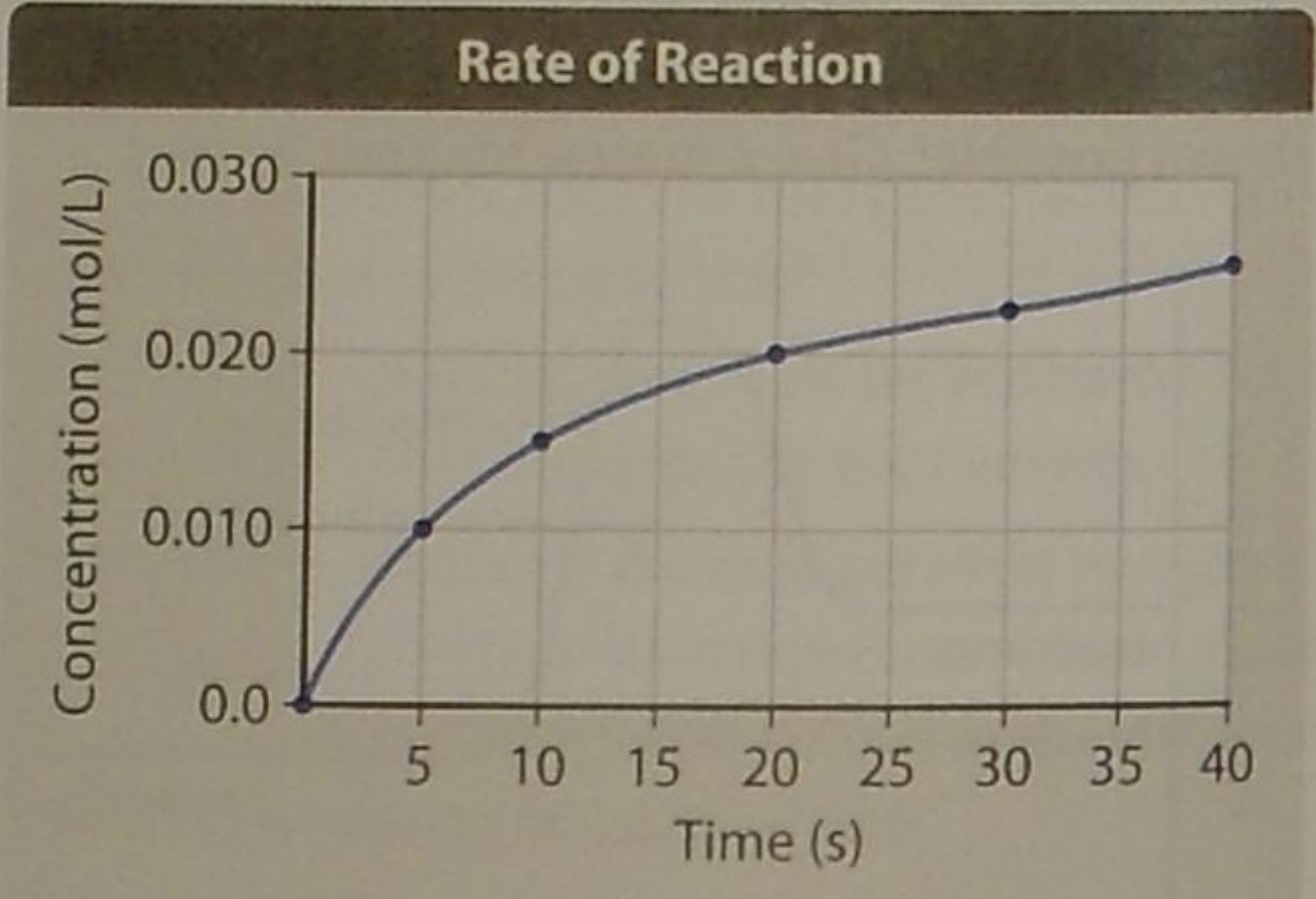
$$Fe(s) + 2AgNO_3(aq) \rightarrow Fe(NO_3)_2(aq) + 2Ag(s)$$

Over a period of 25.0 min, the concentration of a $AgNO_3(aq)$ solution decreases from 0.200 mol/L to 0.185 mol/L.

a. What is the rate of change in the concentration of $Ag^+(aq)$ measured in moles per litre per second?

b. What is the rate of formation of $Fe^{2+}(aq)$ over this same period of time?

42. A graph of concentration vs. time is shown below. Reproduce this graph in order to determine the instantaneous rates of reaction at $t = 0$ s and $t = 30.0$ s and the average rate of reaction from $t = 0$ s to $t = 30.0$ s.



43. For reaction 1, $\Delta H = -50$ kJ and $E_{a(fwd)} = +25$ kJ. For reaction 2, $\Delta H = +50$ kJ and $E_{a(rev)} = +25$ kJ. Compare the value of $E_{a(fwd)}$ for reaction 2 with the $E_{a(rev)}$ for reaction 1.

44. An average rate of reaction for the consumption of $BrO_3^-(aq)$ is 1.28 g/L·s, in the reaction shown below:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(\ell) + 3H_2O(\ell)$$

What is the average rate of formation of $Br_2(\ell)$?

45. The reaction mechanism outlined below occurs in an aqueous solution to which a small amount of ethanol has been added. The ethanol does not participate in the reaction but is added because of its properties as a solvent. $I_2(s)$ dissolves in alcohol to give a reddish-brown solution.

Step 1: $H_2O_2(aq) + I^-(aq) \rightarrow HIO(aq) + OH^-(aq)$ (slow)

Step 2: $OH^-(aq) + H^+(aq) \rightarrow H2O(\ell)$ (fast)

Step 3: $HIO(aq) + H^+(aq) + I^-(aq) \rightarrow I_2(aq) + H_2O(\ell)$ (fast)

a. What is the overall equation that is represented by this reaction mechanism?

b. Suggest two properties that could be used to monitor the rate of reaction over time. Explain your choices of properties.

46. Consider the reaction mechanism outlined below:

Step 1: $H_2(g) + NO(g) \rightarrow H_2O(g) + N(g)$ (fast)

Step 2: $N(g) + NO(g) \rightarrow N_2O(g)$ (slow)

Step 3: $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$ (fast)

a. Is a catalyst present? Give a reason for your answer.

b. Identify the intermediates in the reaction.

c. Write the overall reaction equation.

47. The rate law for a reaction is rate $= k[A]^{\frac{1}{3}}$. Determine the unit for the rate constant.

48. Distinguish between the meaning of the terms *reaction intermediate* and *catalyst*, using the two-step reaction mechanism shown below. Write the overall balanced chemical equation for the reaction.

Step 1: $Fe^{3+}(aq) + 2I^-(aq) \rightarrow Fe^{2+}(aq) + I_2(aq)$

Step 2: $S_2O_8^{2-}(aq) + Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + Fe^{3+}(aq)$

49. At 950 K and a pressure of 70.0 kPa, the rate of formation of hydrogen gas, $H_2(g)$, is 4.8×10^{-3} mol/L·s. If all gases are measured at this same temperature and pressure, at what rate will phosphine, $PH_3(g)$, be consumed?

$$PH_3(g) \rightarrow P(g) + \frac{3}{2}H_2(g)$$

50. For the reaction below, the rate doubles if [NO] doubles and quadruples if $[H_2]$ doubles.

$$NO(g) + H_2(g) \rightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2O(g)$$

a. What is the rate law for this reaction?

b. How will the rate of reaction be affected if both [NO] and $[H_2]$ double at the same time?

51. Apply Hess's law using the equations below to determine the enthalpy change for the following reaction:

$$2H_3BO_3(aq) \rightarrow B_2O_3(s) + 3H_2O(\ell)$$

(1) $H_3BO_3(aq) \rightarrow HBO_2(aq) + H_2O(\ell)$ $\Delta H^\circ = -0.020$ kJ

(2) $2B_2O_3(s) + H_2O(\ell) \rightarrow H_2B_4O_7(s)$ $\Delta H^\circ = -17.5$ kJ

(3) $H_2B_4O_7(s) + H_2O(\ell) \rightarrow 4HBO_2(aq)$ $\Delta H^\circ = -11.3$ kJ

52. The table below shows rate of reaction data for the following reaction:

$$2A + B \rightarrow A2B$$

Data

Experiment	Initial Concentration of A (mol/L)	Initial Concentration of B (mol/L)	Initial Rate (mol/L·s)
1	0.46	0.34	1.32
2	0.92	0.34	2.64
3	0.46	1.02	3.96

a. Use this information to determine the rate law expression for the reaction.

b. What is the overall order of the reaction?

Communication

53. The decomposition of magnesium carbonate, $MgCO_3(s)$, occurs according to the following reaction:
$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$ $\Delta H_r = +117.3$ kJ
Sketch an enthalpy diagram for the reaction.

54. Outline how you would use a simple laboratory heating device, such as an alcohol lamp or Bunsen burner, to demonstrate the difference between potential energy and kinetic energy.

55. A classmate is having difficulty understanding why, when using thermochemical data to calculate energy changes for a change of state, ΔH_{fre} is a negative value. In one or two sentences, provide an explanation that is at a level that could help your classmate understand this concept.

56. *Enthalpy change* is a term that is used for more than one application. Use a concept map to summarize and indicate the difference between the different uses of the ΔH notation.

57. Research the use of catalysts in the refining of crude oil. Write a one-page report that outlines the cracking, reformation, and isomerization processes and how catalysts are used in these processes.

58. BIG IDEAS Technologies that transform energy can have societal and environmental costs and benefits. Draw a flowchart to represent the production of $NH_3(\ell)$ in the Haber-Bosch process.

59. Platinum is used as a catalyst in many processes. Research the use of this metal as a catalyst. Using diagrams with descriptive captions, summarize key information about three industrial processes in which platinum is used. Your summary should indicate the characteristics of platinum that make it useful as a catalyst, and include the names of the processes or reactions and the reactants and products in the reactions.

60. Consider the following reaction:

$$2X + 3Y + 45\text{ kJ} \rightarrow 3Z$$

Prepare a presentation to illustrate to your class that this reaction cannot proceed in the way the balanced equation indicates. List the points you would include in the presentation. What is a more likely occurrence for this reaction?

61. Using a graphic organizer, summarize information about rates of reaction in terms of the following: *reaction mechanism, rate-determining step, overall rate, role of a catalyst, activation energy*, and *order of a reaction.*

62. Develop a graphic representation to illustrate how the number of particles present at two different concentrations can explain why an increase in concentration results in an increase in the rate of reaction. Be sure to label both *x*- and *y*-axes, and specify which graph represents which concentration. Also, indicate the part of the graphic that represents the activation energy, E_a.

63. The initial concentration for $P_2Q(aq)$ is 0.25 mol/L in the reaction shown below:

$$G(s) + P_2Q(aq) \rightarrow GQ(aq) + 2P(s)$$

All of $P_2Q(aq)$ is consumed in the reaction. Using an appropriate scale, sketch a graph of concentration vs. time that would show changes in the concentrations of the reactants and products in aqueous solution.

Application

64. Aluminum is a reactive, self-protecting metal used to make doors, windows, and siding for houses. It reacts quickly with $O_2(g)$ to form an impervious coating of aluminum oxide, $Al_2O_3(s)$, that prevents $O_2(g)$ from reacting any further with the aluminum. This reaction is unnoticeable even though the reaction shown below indicates a large enthalpy change. Why is the enthalpy of reaction not detectable?

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s) + 3351.4\text{ kJ}$$

65. Pieces of three different metals, each having a mass of 12.5 g, are warmed to 150.0°C in an oil bath. They are individually transferred to 100.0 mL of water that is initially at 20.0°C. The final temperature of the water is recorded in the table below.

Data

Metal	Final Temperature (°C)
1	21.5
2	23.4
3	21.7

a. Why is the final temperature of the water different for each metal?

b. Calculate the specific heat capacity of each metal, and use the data in **Table 5.1** to identify the three metals.

66. There are many common examples of reactions that are beneficial to use by increasing the rate of reaction. Compile a list of at least four reactions that are of benefit to our everyday living, in which a *reduction* in the rate of reaction is desired.

67. **BIG IDEAS** Energy changes and rates of chemical reactions can be described quantitatively. A butane burner is used to heat a pot of water at a camp site. The efficiency of heat transfer from the flame is 45.0%.

a. Use the data below to calculate the mass of butane that must be burned to bring the water to 100.0°C.

mass of water = 882 g

$c_{H_2O(\ell)} = 4.19\text{ J/g}\cdot°\text{C}$

initial temperature of water = 15.0°C

final temperature of water = 100.0°C

mass of iron pot = 1208 g

$c_{iron} = 0.449\text{ J/g}\cdot°\text{C}$

$\Delta H^\circ_{comb}\ (C_4H_{10}) = -2877.6\text{ kJ/mol}$

b. If it takes 1 hour and 15 minutes to heat this water, at what rate, in moles per minute, is the butane burned?

68. **BIG IDEAS** Efficiency of chemical reactions can be improved by applying optimal conditions. Acetylene is used as a fuel for a torch to cut through metal. When a worker first lights the torch, the flame is orange and there is noticeable black soot. To use the torch for cutting, the acetylene-air mixture is adjusted and the flame becomes blue and much hotter.

a. What type of combustion is occurring when the fuel is first lit compared with when it is used to cut through metal?

b. Compare the enthalpy change for the complete combustion and the incomplete combustion of acetylene, $C_2H_2(g)$, using the equations below and the enthalpies of formation listed in Appendix B.

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(g)$$

$$C_2H_2(g) + O_2(g) \rightarrow \frac{1}{2}CO_2(g) + \frac{3}{2}C(s) + H_2O(g)$$

c. Compare the availability of chemical energy from acetylene for complete combustion vs. incomplete combustion.

69. Ethylene, $C_2H_4(g)$, can be converted to ethanol, $C_2H_5OH(\ell)$, with an efficiency of 95% using a phosphoric acid catalyst. Use Hess's law to determine the enthalpy of reaction for the equation shown below:

$$C_2H_4(g) + H_2O(\ell) \rightarrow C_2H_5OH(\ell)$$

(1) $C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$ $\quad \Delta H = -1367 \text{ kJ}$

(2) $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(\ell)$ $\quad \Delta H = -1411 \text{ kJ}$

70. Nitryl chloride, NO_2Cl, is a strong oxidizing agent and a potential pollutant in the upper atmosphere. Research conducted to gather data about this molecule has proposed the following mechanism for its formation. The first and last steps in the mechanism and the overall reaction are shown below:

Step 1: $NO_2 + Cl_2 \rightarrow NO_2Cl_2$

Step 2:

Step 3: $Cl + NO_2 \rightarrow NO_2Cl$

Overall: $2NO_2 + Cl_2 \rightarrow 2NO_2Cl$

a. What is the equation for step 2?

b. How do you know which species is an intermediate? Identify the intermediate(s) in the mechanism.

c. Is step 2 likely the slow step in the mechanism? Give a reason for your answer.

d. Research the use of nitryl chloride and provide a summary of its harmful effects on the environment. Based on your research, propose an argument either for or against its use. Be sure to include supporting points for your argument.

71. You are performing an investigation that involves the reaction represented below:

$$2A + B \rightarrow \text{products}$$

For this reaction, the following information is known:

rate law: rate $= k\,[A][B]$

original concentration of A = 0.40 mol/L

original concentration of B = 0.60 mol/L

rate of reaction = 4.5×10^{-2} mol/L·s, at 35°C

You have completed one trial. You decide for the second trial to use twice the concentration of reactant A.

a. Explain why the concentration of B must also change if the rate of reaction is to be unchanged at this temperature.

b. If the rate of reaction is to be the same as in the first trial, what concentration of reactant B must be used?

c. Calculate the value of the rate constant.

d. Confirm your answer to part (b) by calculating the rate law, using the new values for [A] and [B].

72. Graphs of rate of reaction vs. concentration for two reactions are plotted. Each is a straight line but one has a steeper slope. What can be concluded about the rates of these reactions?

73. **BIG IDEAS** Energy changes and rates of chemical reactions can be described quantitatively.

Hydrogen peroxide is used as an antiseptic and antibacterial agent. In the bottle and on our skin, it breaks down very slowly but it does not foam. On a scrape or a cut, bubbling action is observed as the hydrogen peroxide decomposes rapidly in the presence of a catalyst.

$$H_2O_2(aq) \rightarrow H_2O(\ell) + \frac{1}{2}O_2(g)$$

a. Using print or Internet sources, identify the catalyst that causes this action.

b. Use the molar enthalpy of formation data in Appendix B to determine the enthalpy change for this decomposition.

c. The activation energy for the uncatalyzed decomposition of hydrogen peroxide has been measured at 25°C to be 75 kJ/mol. Sketch a potential energy diagram, using an appropriate scale, to show $E_{a(fwd)}$ and ΔH. If it is estimated that there will 80% more collisions that are effective in the presence of the catalyst, show the path of the catalyzed reaction on the potential energy diagram.

d. What is ΔH for the reverse reaction? Does this quantity represent the enthalpy of formation, ΔH_f, for hydrogen peroxide? Give a reason for your answer.

74. For a reaction that occurs in the gaseous phase, the rate of reaction doubles when the concentration of reactant X is doubled. There is no change in the rate of reaction when the concentration of reactant Y is changed.

$$2X + \frac{1}{2}Y \rightarrow W + 2Z$$

If the volume of the container is doubled, what change would be expected in the rate of reaction? Give an explanation for your answer.

UNIT 3 SELF-ASSESSMENT

Select the letter of the best answer below.

1. **K/U** The enthalpy change in a reaction comes from the
   a. difference between the kinetic energy of the products and the reactants.
   b. sum of the potential energies of the reactants and products.
   c. sum of the thermal energies of the reactants and products.
   d. sum of the enthalpies of formation of the reactants and products.
   e. difference in the energy added for breaking bonds in the reactants and the energy given off when bonds are formed in the products.

2. **T/I** Use the given equations to determine the enthalpy change for the reaction below:

$$2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$$

   (1) $S(s) + O_2(g) \rightarrow SO_2(g) \quad \Delta H^\circ_{comb} = -296.8\ kJ$
   (2) $S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g) \quad \Delta H^\circ_{comb} = -395.7\ kJ$
   a. −98.9 kJ
   b. +346.2 kJ
   c. −49.4 kJ
   d. +197.8 kJ
   e. +692 5 kJ

3. **T/I** What is the enthalpy of reaction per mole of HCl(g) for the reaction below?

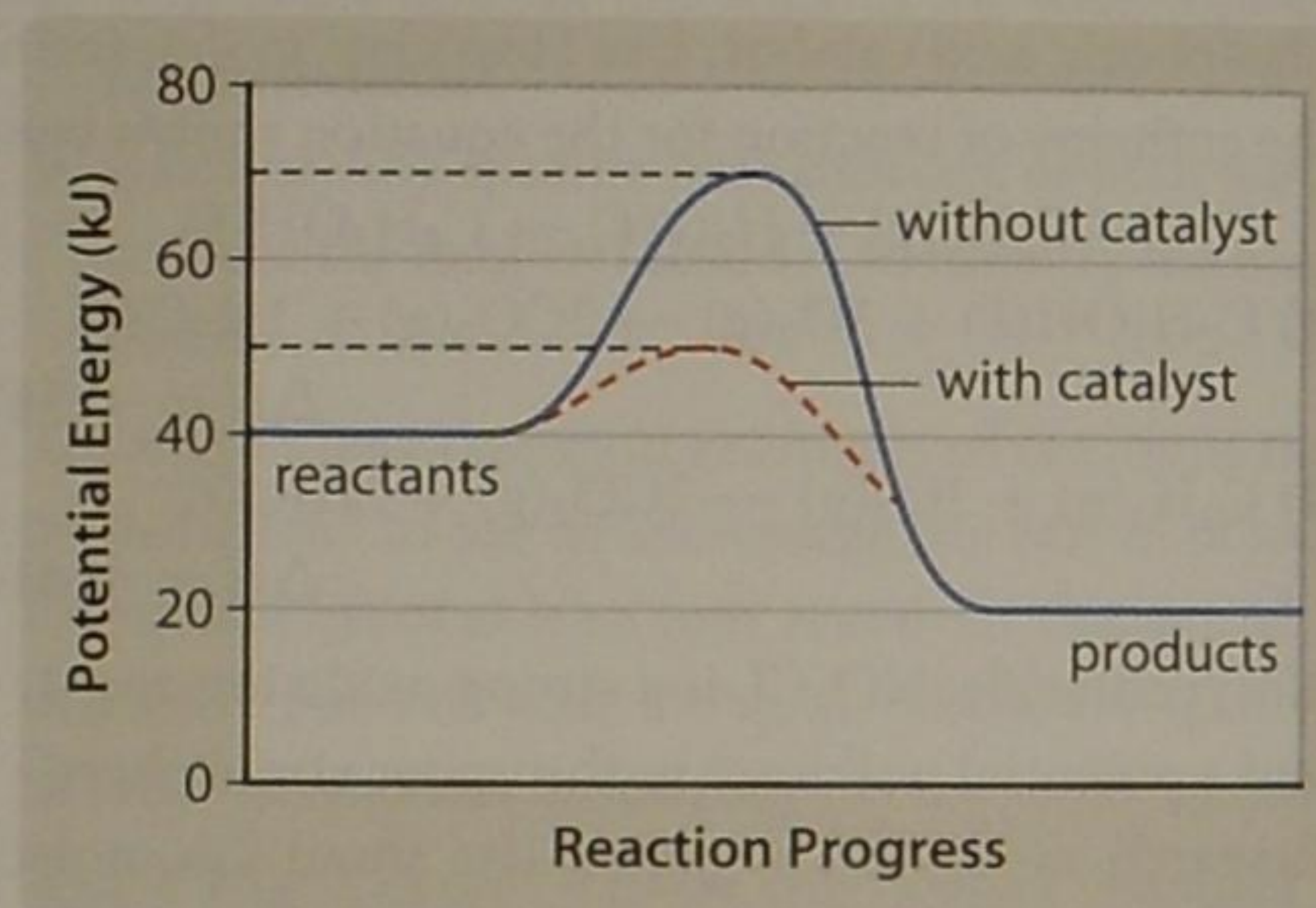
   $4HCl(g) + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O(g) + 114.4kJ$
   a. −457.6 kJ/mol
   b. −114.4 kJ/mol
   c. −28.6 kJ/mol
   d. +114.4 kJ/mol
   e. +57.2 kJ/mol

4. **T/I** The temperature of a calorimeter increases from 15.6°C to 31.4°C as it gains 488.8 kJ of heat. What is the heat capacity of the calorimeter?
   a. 489 kJ/°C
   b. 30.9 kJ/°C
   c. 31.3 kJ/°C
   d. 10.4 kJ/°C
   e. 15.6 kJ/°C

5. **A** A sample of butane, $C_4H_{10}(g)$, having a mass of 0.58 g was completely combusted to produce carbon dioxide, water vapour, and 27 kJ of thermal energy. Which thermochemical equation correctly shows this information per mole of $C_4H_{10}(g)$?
   a. $C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g) + 2700\ kJ$
   b. $C_4H_{10}(g) + 13O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g) + 270\ kJ$
   c. $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g) + 2700\ kJ$
   d. $2C_4H_{10}(g) + O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g) + 5400\ kJ$
   e. $C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g) + 27\ kJ$

6. **A** The rate law for a particular reaction is first order with respect to two reactants. If the concentrations of both reactants are doubled, the rate of the reaction would be expected to
   a. double.
   b. not change.
   c. triple.
   d. quadruple.
   e. increase by a factor of 1.5 .

7. **A** Which statement regarding the potential energy diagram below is correct?



   a. The activation energy for the uncatalyzed reaction in the forward direction, $E_{a(fwd)}$, is +20 kJ.
   b. For the catalyzed reaction in the reverse direction, ΔH_{rev} is +20 kJ.
   c. The potential energy of the activated complex for the catalyzed reaction is +70 kJ.
   d. The catalyst lowers the activation energy of both the forward and reverse reactions by 30 kJ.
   e. For the uncatalyzed reaction in the forward direction, ΔH_{fwd} is +20 kJ.

8. **T/I** For the decomposition of potassium chlorate, $KClO_3(s)$, 4.4 g of this compound reacted in 2.3 min. What is the average rate of reaction in moles per second?
   a. 1.7
   b. 3.2×10^{-2}
   c. 1.6×10^{-2}
   d. 2.6×10^{-4}
   e. 5.9×10^{-4}

9. **K/U** Which reaction is most likely to occur rapidly at room temperature?
   a. $Zn(s) + S(\ell) \rightarrow ZnS(s)$
   b. $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2(g)$
   c. $H_2O(\ell) \rightarrow H_2 + \frac{1}{2}O_2(g)$
   d. $2Fe(s) + 2H_2O(\ell) + O_2(g) \rightarrow 2Fe(OH)_2(s)$
   e. $Cd(s) + NiO_2(s) + 2H_2O(\ell) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$

10. T/I A hypothetical reaction mechanism is outlined below. For which substance(s) would a change in concentration have the greatest effect on the overall reaction rate?

Step 1: $2A \rightarrow B + 2C$ (slow)

Step 2: $B + C \rightarrow E$ (fast)

Step 3: $C + D \rightarrow F$ (fast)

a. A + D
b. D
c. A
d. B + C
e. C

Use sentences and diagrams, as appropriate, to answer the questions below.

11. K/U What information is given by the equation below?

$Cu(s) + Cl_2(g) \rightarrow CuCl_2(s) \qquad \Delta H^\circ_r = -220.1\ kJ$

12. T/I The standard molar enthalpy of formation, ΔH°_f, for liquid benzene, $C_6H_6(\ell)$, is +49.1 kJ/mol and for benzene vapour, $C_6H_6(g)$, is +82.9 kJ/mol. Apply Hess's law to determine the standard molar enthalpy of vaporization, ΔH°_{vap}, for benzene.

13. K/U What assumptions are made when using a simple calorimeter?

14. C Your lab partner writes the equation for the enthalpy of formation, ΔH°_f, for $CO_2(g)$ as the following:

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

How would you explain that this is incorrect? Write the correct enthalpy of formation equation.

15. A Air temperature is observed to increase when a rain shower occurs. What amount of thermal energy is given off into the air when 9.83×10^{10} kg of water vapour condenses?

16. T/I Calculate the amount of heat given off when 1 mol $SO_2(g)$ forms in the reaction as written below:

$$CS_2(\ell) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$$

17. T/I A 250.0 g sample of ethanol is heated until its temperature increases by 30.0°C. If 27.3 kJ of thermal energy was added to the sample, how efficient was the heat transfer? The specific heat capacity of ethanol is 2.44 J/g·°C.

18. A The following reaction is performed in duplicate:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$

In the first trial, the volume ratio used for $H_2(g):O_2(g) = 2:1$. In the second trial, the volume ratio used for $H_2(g):O_2(g) = 1:1$. For each trial, sketch a graph of concentration vs. time, for the reactants only, as the reaction proceeds to completion.

19. C The following decomposition reaction occurs:

$$2HgO(s) \rightarrow 2Hg(\ell) + O_2(g)$$

When the heat source is removed, the decomposition stops. The reaction begins again when the heat source is turned on. Develop a 2 to 3 min oral presentation that explains these observations.

20. K/U Reactions between ions in aqueous solution to form a precipitate occur in an instant at room temperature. Does this mean that, for these reactions, $E_a = 0$? Explain your reasoning.

21. C Develop a flowchart that summarizes how to use Hess's law to determine the enthalpy change of a reaction. Include an example.

22. T/I Examine the following reaction mechanism:

Step 1: $NO_2(g) + Br_2(g) \rightarrow NO_2Br(g) + Br(g)$ (slow)

Step 2: $NO_2(g) + Br(g) \rightarrow NO_2Br$ (fast)

a. What is the overall reaction?
b. Which is the rate-determining step?
c. If rate = $k[NO_2][Br_2]$, what is the order of the reaction with respect to $Br_2(g)$?

23. T/I For the reaction mechanism shown below, the rate law is rate = $k[NO]^2[O_2]$. Is the proposed mechanism possible for this rate law? Explain.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Step 1: $2NO + O_2 \rightarrow N2O_4$ (fast)

Step 2: $N_2O_4 \rightarrow 2NO_2$ (slow)

24. K/U Compare the energy changes associated with physical, chemical, and nuclear processes. Give one example of each process.

25. K/U Summarize the projected use of renewable energy sources in Ontario by 2025. Describe the advantages and disadvantages of these energy sources.

Self-Check

If you missed question ...	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Review section(s)...	5.1 5.2	5.3	5.2	5.2	5.2	6.3	6.2	6.1	6.3	6.3	5.2	5.3	5.2	5.3	5.1	5.3	5.4	6.1	6.2	6.2	5.3	6.3	6.3	5.1	5.4